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Reconstructing Late Holocene Hydrographic Variability of the Gulf of Maine

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RECONSTRUCTING LATE HOLOCENE HYDROGRAPHIC VARIABILITY OF THE GULF OF MAINE

By

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By Nina Millicent Whitney

Thesis Advisor: Karl Kreutz

An Abstract of the Thesis Presented
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I present an annually resolved reconstruction of seawater temperatures in the western North Atlantic from 1695-1915. This paleoclimate record was constructed using oxygen isotopes measured in precisely dated *Arctica islandica* shells collected off of Seguin Island in the western Gulf of Maine. The temperature reconstruction was derived from this oxygen isotope time series using a modern $\delta^{18}O_w$-salinity mixing line developed for coastal waters in the Gulf of Maine from water samples collected over the last decade. The $\delta^{18}O_w$ and salinity composition of these water samples indicate that coastal surface waters consist of a mixture of Scotian Shelf Water and Maine River Water. The properties of these coastal waters are significantly influenced by seasonal changes in local river discharge.

The Gulf of Maine oxygen isotope record suggests centennial-scale oscillations in seawater temperatures and therefore in the strength and position of the major ocean current systems that influence Gulf of Maine water properties. This record indicates that recent warming seen in the Gulf of Maine is not yet outside the natural seawater

temperature variability of the region and therefore cannot be unequivocally linked to anthropogenic climate change.

The positive and negative correlations between the Gulf of Maine oxygen isotope record and seawater temperature records from the subpolar gyre region of the North Atlantic and the western North Atlantic, respectively, are similar in pattern to the modeled and observed influence of the Atlantic meridional overturning circulation (AMOC) on seawater temperatures in these regions. This similarity suggests a possible association between AMOC variability and seawater temperatures in the Gulf of Maine. The association indicates that seawater temperature reconstructions from oxygen isotopes measured in *A. islandica* shells collected in the Gulf of Maine could provide an annually resolved, precisely dated reconstruction of AMOC variability. The oxygen isotope record I present in this thesis suggests centennial-scale oscillations in AMOC variability, with increased strength of the AMOC after the Little Ice Age.

DEDICATION

This thesis is dedicated to my amazing twin sister, Holly Jean Whitney, who is literally my other half. I can't even begin to put into words all that Holly means to me and why I couldn't have done any of this without her. But Holly already knows: she is my twin, after all.

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Thank you to my other University of Maine friends who have supported me along the way. I am so lucky to have made friends that I will be able to count on even after I have left the University of Maine.

I could not have done any of this without my incredible family. Thank you to my grandfathers for their undying support. Thank you to Pop for the incredible opportunities that he gave and continues to give me in my education and in my life. Thank you to the Old One, whose curiosity for learning and for science and whose persistent questions are a large part of the reason that I decided to become a scientist. And of course, thank you to my parents and to my twin sister. I consider myself one of the luckiest people alive to have a family as close and as supportive as the one I have. They are everything to me and I could not have done any of this without them. I won't always be your little girl but I will always be your little girl.

Last, but certainly not least, thank you to the many ocean quahogs who sacrificed their lives, potentially unknowingly, for my research. I think it's time for me to clam up now and let them tell the story of past climate in the Gulf of Maine.

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LIST OF ABBREVIATIONS

AMO Atlantic Multidecadal Oscillation

AMOC Atlantic meridional overturning circulation

AO Arctic Oscillation

ARW Arctic River Water

EMCC Eastern Maine Coastal Current

ERSST Extended Reconstructed Sea Surface Temperature

GMCC Gulf of Maine Coastal Current

ITCZ Intertropical Convergence Zone

LIA Little Ice Age

LShW Labrador Shelf Water

LSW Labrador Slope Water

MAB Mid-Atlantic Bight

MCA Medieval Climate Anomaly

MRW Maine River Water

NAO North Atlantic Oscillation

NERACOOS Northeastern Regional Association of Coastal and Ocean Observing Systems

SLEW St. Lawrence Estuary Water

SLRW St. Lawrence River Water

SST Sea surface temperature

SSW Scotian Shelf Water

WMCC Western Maine Coastal Current

WSW Warm Slope Water

Chapter 1
INTRODUCTION

The 100 year projection for increases in greenhouse gases, temperature, sea level, storm intensity, et cetera suggest significant changes to global climate (IPCC, 2013). However, due to the immense complexity of the climate system, there is still a significant amount that is unknown about what the climate response to increasing greenhouse gases will be and how this response will affect various organisms, species, ecosystems and regions around the world, as well as human society in general. Therefore, it is imperative to study the climate system from a variety of perspectives in order to understand better, among other characteristics, the natural variability of the system and major drivers and feedbacks.

One area of climate research that is vital in gaining this in-depth understanding is paleoclimatology. Because reliable instrumental data have only been kept for little over 100 years, it is difficult to determine natural variability in climate systems, especially those systems that are influenced by multidecadal to centennial scale climate oscillations. It is also difficult to understand climate drivers and feedbacks in certain regions with such a short record. Paleoclimate research uses proxy data from a variety of sources, including tree rings, corals, ice cores, glacial deposits, sediment cores, speleothems, other carbonate and silicious materials and faunal assemblages to reconstruct climate in the past. These long-term records of climate in regions around the world allow for a better comprehension of climate dynamics, enabling more accurate and precise climate predictions. It is only with these climate predictions that mitigation strategies and adaptation measures based on these predictions can start to combat the climate changes already being observed on the planet.

In this thesis, I present an annually resolved reconstruction of climate and hydrographic variability in the Gulf of Maine, a semi-enclosed basin in the western North Atlantic, on the east coast of North America. The following introduction is meant to provide a brief overview of Holocene climate and climate dynamics in the North Atlantic as well as an introduction to the Gulf of Maine as a geographically important region for reconstructing high resolution climate records in the North Atlantic. An overview of the proxy and reconstruction techniques used in this thesis is also included.

1.1 The North Atlantic

The North Atlantic is a particularly important region of the world in which to study past climate. This area of the ocean is crucial to climate dynamics as it has significant influence on global heat exchange (Levitus et al., 2000; Manabe and Stouffer, 1999*a*; Visbeck, 2002) and plays a large role in regulating the earth's carbon budget by acting as a major atmospheric CO_2 sink (Sabine et al., 2004). These characteristics are in part due to the formation of deep water in the Labrador Sea and east of Greenland which drive the Atlantic meridional overturning circulation (AMOC), the global "ocean conveyor" that transports ocean waters around the earth (Broecker et al., 1985). Changes in the AMOC have a large impact on global climate, including temperature distribution in the North Atlantic, and have been implicated as the cause for several large-scale abrupt climate changes in the Northern Hemisphere in the past (Barber et al., 1999; Broecker et al., 1985; McManus et al., 2004; Murton et al., 2010). In addition to the AMOC, there are also several important coupled ocean-atmosphere climate oscillations in the North Atlantic that have been shown to regulate Northern Hemisphere climate on a variety of time scales, including the North Atlantic Oscillation (NAO) and the Atlantic Multidecadal Oscillation (AMO) (Figure 1.1). Therefore, it is vital to reconstruct climate in the North Atlantic, both to understand the natural variability of the system as well as some of the dynamics behind the drivers of Northern Hemisphere climate.

1.1.1 Drivers of North Atlantic climate

It has long been understood that changes in sea surface temperatures (SSTs) in the North Atlantic play a large role in regulating regional climate. Bjerknes (1964) was one of the first to address the drivers of North Atlantic SST variability. He argued that on short, annual time scales, local atmospheric forcings regulated the variation in SSTs but that on interdecadal and multidecadal time scales, ocean circulation is largely responsible for oscillations in SSTs. This oscillation in ocean temperatures is now known as the AMO (Figure 1.1).

The AMO is an index of the observed oscillation in average SST anomalies in the North Atlantic. The exact calculation of the AMO varies. Trenberth and Shea (2006) defined the AMO as the average SST between 0°-60°N, 0°-80°W minus average SSTs between 60°S-60°N. Alternatively, van Oldenborgh et al. (2009) chose to not consider the tropical region because of the influence of the El Niño Southern Oscillation on this region and defined the AMO as the average SST between 25°-60°N, 7°-70°W minus the regression on global mean temperature. The two different definitions agree very well on longer time scales, although do show differences on monthly and interannual time scales.

The AMO has been observed in the North Atlantic since the beginning of the instrumental record in 1856 (Folland et al., 1984, 1986; Kushnir, 1994; Kushnir et al., 1997; Tourre et al., 1999) with an amplitude of ~0.4°C (Dima and Lohmann, 2007) and a periodicity of ~70 years (Delworth and Mann, 2000). While it is most prominent in the North Atlantic, there is also a positively correlated oscillation in the North Pacific, suggesting a link between the two oscillations, likely through at-

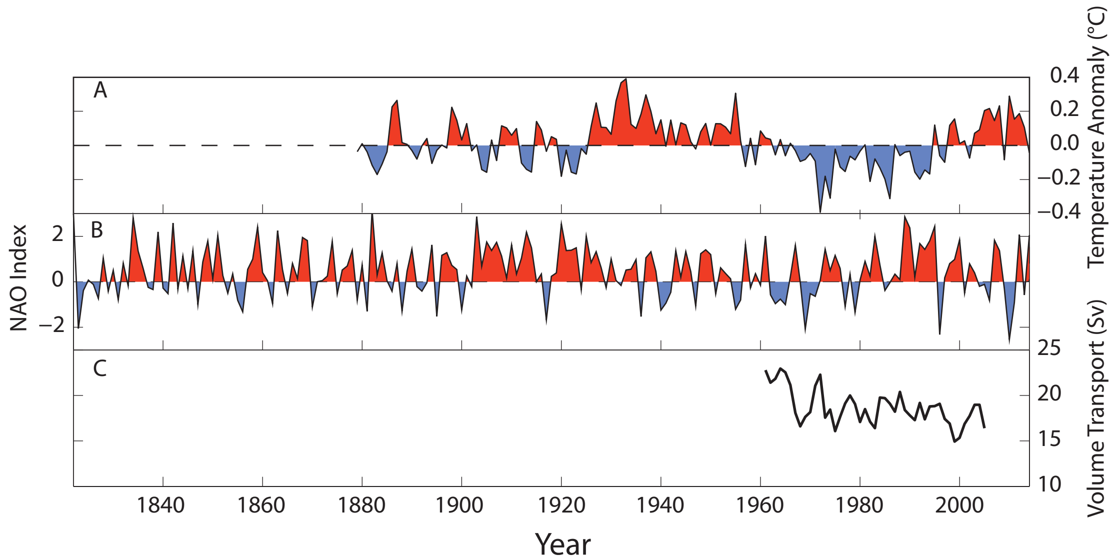

Figure 1.1. Instrumental and reanalysis time series' of North Atlantic climate drivers. (A) The Atlantic Multidecadal Oscillation (AMO) shown by sea surface temperature anomalies in the North Atlantic (defined here as 0°-60°N, 0°-60°W) after subtracting the annual average SST from 60°S-60°N to account for global changes in temperature not associated with the AMO. Data from Hadley Centre Sea Ice and Sea surface Temperature dataset (HADISST; Rayner et al., 2003). (B) The North Atlantic Oscillation (NAO) shown by the normalized index of the difference in winter (December - March) sea level pressure between southwest Iceland and Gibraltar from Jones et al. (1997) and updated by Osborn (2011). While the NAO is generally considered to be the difference in sea level pressure between Iceland and the Azores, Gibraltar sea level pressure has been shown by Jones et al. (1997) to have a strong correlation with Azores sea level pressure. Because instrumental records of sea level pressure go back farther in Gibraltar, using this location provides a longer instrumental record of the NAO. (C) Annual average of the Atlantic meridional overturning circulation (AMOC). Data from ECMWF operational ocean reanalysis system 3 at 26°N. This data is an integration of zonal-mean velocity from 1200 meters to the sea surface obtained using data assimilation techniques, which combine ocean model results and observations (Balmaseda et al., 2007). The AMOC is hard to measure with instruments and therefore long-term instrumental data for the AMOC is nonexistent.

mospheric teleconnections (Dima and Lohmann, 2007; Enfield et al., 2001; Minobe, 1997). The AMO influences North American and European climate in a variety of ways (Knight et al., 2006; Sutton and Hodson, 2005). It correlates with European winter air temperatures and the Sahel drought (Folland et al., 1986), western European and North American precipitation patterns (Enfield et al., 2001), Atlantic Ocean hurricane formation (Goldenberg et al., 2001) and glacial extent in the Swiss Alps (Denton and Broecker, 2008).

Since Bjerknes first suggested the relationship between SSTs and ocean circulation, numerous authors have used primarily ocean models to conclude that the AMOC is in fact driving these multidecadal oscillations in temperature (Delworth et al., 1993; Kushnir, 1994; Stocker and Mysak, 1992; Timmermann et al., 1998). The suggested AMOC influence on the AMO is fairly straightforward. During a strong (weak) AMOC, more (less) warm water is transported up from the tropics towards the poles, creating positive (negative) SST anomalies in the North Atlantic. However, there is a lack of empirical evidence to suggest such a relationship between the AMO and the AMOC. Therefore, the climate drivers of the AMO are still unclear.

Additionally, it is unclear what drives variability in the AMOC on a variety of time scales. This AMOC variability has been explained both by internal atmospheric oscillations on interdecadal time scales and by coupled ocean-atmosphere dynamics on longer, multidecadal time scales. Both mechanisms involve the NAO. The NAO is an index of the anomalous difference in atmospheric sea level pressure between the Icelandic low atmospheric pressure zone and the Azores high atmospheric pressure zone over the North Atlantic (Hurrell, 1995) and is closely related to North Atlantic storm track patterns (Ulbrich and Christoph, 1999). The NAO, which exists throughout the year but is most dominant in the winter due to the more persistent presence of a low pressure system near Iceland during this time of the year, has been correlated with variability in atmospheric circulation, air temperature, precipitation and oceanic circulation.

Several authors have suggested that interdecadal variability in the AMOC is due to internal variability in the NAO. Delworth and Greatbatch (2000) use a Geophysical Fluid Dynamics Laboratory climate model to show that variability in the AMOC is largely driven by surface heat fluxes regulated by internal variability of the NAO instead of freshwater or momentum fluxes. Eden and Jung (2001) used an ocean general circulation model to show that the NAO is a main driver of the AMOC by regulating net surface heat fluxes in the northwestern North Atlantic. This association occurs because a positive (negative) mode of the NAO is associated with increased (decreased) strength of the westerly winds. Variation in the strength of the westerly winds affects the heat flux and the amount of convection in the Labrador Sea and therefore the amount of Labrador deep water formation (Dickson et al., 1996; Eden and Jung, 2001; Ortega et al., 2011). This relationship is confirmed by additional model studies that suggest that NAO related variations in heat flux in the Labrador Sea lead to a 2-3 year lagged response of the AMOC (Eden and Willebrand, 2001; Häkkinen, 1999).

Dong and Sutton (2005) suggest a different mechanism for the NAO's influence on the AMOC, with internal variability of the NAO forcing the system, although the ocean dictates the time scale of the oscillation. During a weak AMOC phase, cold water builds up in the North Atlantic subpolar gyre. Positive modes of the NAO induce increased wind and heat flux, which, along with the cold water anomalies, enhance subpolar gyre circulation and North Atlantic Current strength, bringing saltier waters northward. The buildup of denser waters in areas of deep water formation leads to increased AMOC strength and the opposite phase of the oscillation.

Conversely, other authors have suggested a coupled ocean-atmosphere mechanism through the interaction between the AMOC, the AMO, and the NAO to explain multidecadal variations in the North Atlantic climate. Timmermann et al. (1998) suggest a simplified mechanism to explain this link. Positive SST anomalies caused by increased strength of the AMOC lead to a positive NAO due to latent heat flux. A positive NAO causes reduced evaporation and Eckman transport off of Newfoundland and in the Greenland Sea, as well as reduced surface salinities. This reduction in transport and salinity in turn reduces deep sea convection and deep water formation, thereby reducing the strength of the AMOC. Consequently, less warm water is brought towards the poles. The oscillation then enters its opposite phase. The influence of SSTs on the NAO is supported by modeling work done by Rodwell et al. (1999), that showed that changes in evaporation, precipitation and atmospheric warming due to changes in SSTs led to changes in European storminess, precipitation and atmospheric temperature, all of which influence the mode of the NAO.

The AMOC also appears to be associated with the NAO on shorter, interdecadal time scales. Several authors have demonstrated that changes in the mode of the NAO and Arctic Oscillation (AO), which is defined by pressure gradients in the Arctic and is directly correlated with the NAO, affect the flux of Arctic waters into the Atlantic, which in turn influence the AMOC. During positive NAO/AO modes, waters exit the Arctic through the Canadian Archipelago and into the Labrador Sea. Stronger westerly winds lead to increased heat loss in the Labrador Sea and therefore increased convective mixing. These conditions lead to the increased formation of North Atlantic Deep Water and strength of the AMOC (Dickson et al., 1996). During negative NAO/AO modes, the Transpolar Drift moves to the east and Arctic waters exit through the Fram Straight instead of the Canadian Archipelago (Morison et al., 2012). This influx of freshwater enhances buoyancy driven transport of the East Greenland and West Greenland Currents that flow into the Labrador Sea. The increased buoyancy in the Labrador Sea as well as reduced heat loss and convection resulting from weaker westerly winds leads to decreased Labrador deep water formation. This decreased deep water formation causes a reduction in AMOC strength (Dickson et al., 1996), leading to a cooler climate in the North Atlantic and surrounding regions.

Oscillations in North Atlantic climate on multidecadal to centennial time scales may also be due to internal variability of the AMOC unrelated to the NAO. Vellinga and Wu (2004) suggest an internal mechanism whereby AMOC's effect on the position of the Intertropical Convergence Zone (ITCZ) may induce oscillations in North Atlantic climate. The authors argue that because a strong AMOC causes increased northward ocean heat transport, it creates a cross-equatorial gradient in SSTs. This causes the ITCZ to move northward, bringing increased freshwater flux to the tropical North Atlantic. These fresher waters are gradually brought northward by the AMOC, eventually reaching subpolar North Atlantic waters, where the decreased density from the lower salinity waters weakens AMOC. A weaker AMOC causes a decrease in northward heat transport, which diminishes the cross-equatorial SST gradient, causing the ITCZ to move to the south, reducing tropical North Atlantic freshwater flux and eventually causing an increase in AMOC strength. The oscillation then repeats on multidecadal to centennial time scales.

In summary, while the general drivers of climate variability in the North Atlantic are well known, the specific dynamics, feedbacks and interactions of these drivers are less clear. It is consequently important to continue to analyze and compile detailed reconstructions of North Atlantic climate in the past as these reconstructions enable the investigation of climate variability on a variety of timescales, including those timescales longer than available instrumental records (i.e. multicentennial timescales).

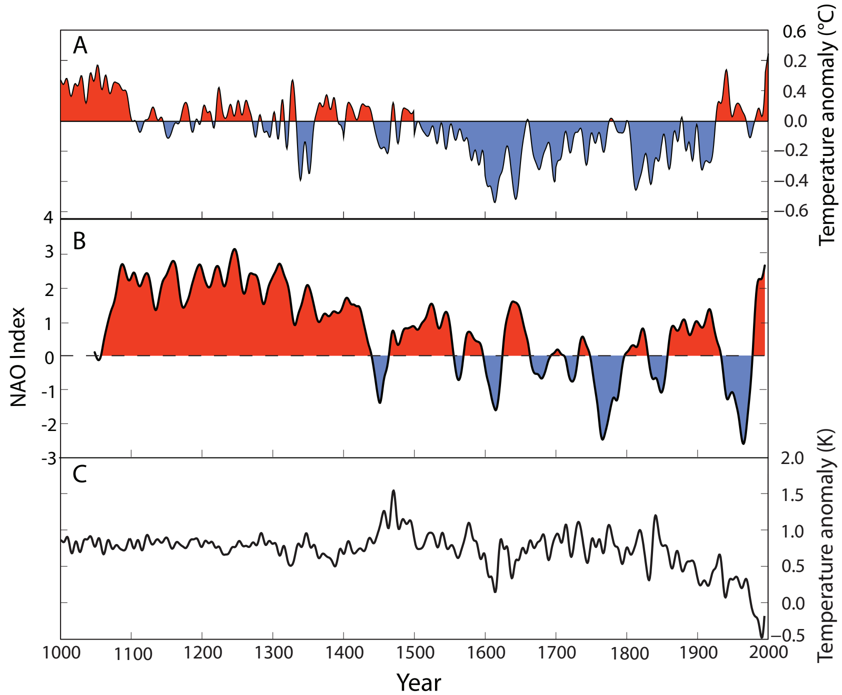

Figure 1.2. Reconstructions of North Atlantic climate drivers over the last 1000 years. (A) Reconstruction of average sea surface temperature anomalies in the North Atlantic using multiple climate proxies from 1000-1850 AD and PC-filtered instrumental records from 1850-2000, from Mann et al. (2009). Red (blue) shaded regions indicate positive (negative) Atlantic Multidecadal Oscillation (AMO) modes. Data fit with a 10-year running average. (B) Reconstruction of the North Atlantic Oscillation (NAO) using speleothems from Trouet et al. (2009). Red (blue) shaded regions indicate positive (negative) NAO modes. Data fit with a 30-year running average. (C) Reconstruction of Atlantic meridional overturning circulation (AMOC) variability. The variability is inferred from the temperature anomaly calculated by subtracting reconstructed Northern Hemisphere temperature from reconstructed subpolar gyre region temperature, with increased temperature anomaly indicating increased AMOC strength. Reconstruction from Rahmstorf et al. (2015). Data are decadally smoothed.

1.1.2 North Atlantic late Holocene climate

There are numerous climate reconstructions throughout the North Atlantic region in a variety of resolutions and on a variety of time scales (Figure 1.2). A review of what these reconstructions suggest about North Atlantic climate in the late Holocene follows.

The Holocene was once thought to be a time of relatively stable interglacial climate in the North Atlantic and the rest of the world. However, more recent work has shown significant oscillations in climate during this time period (Denton and Karlen, 1973; Mayewski et al., 2004), including in the North Atlantic (Bond et al., 1997). The most recent oscillations in North Atlantic/Northern Hemisphere climate are known as the warm period of the Medieval Climate Anomaly (MCA; ~800-1170 AD) and the cold period of the Little Ice Age (LIA; ~1300-1850 AD). A change in the dominant mode of the NAO (from predominantly positive in the MCA to more variable and negative in the LIA; Figure 1.2B) is likely at least partly responsible for the shift in Northern Hemisphere climate recorded in various climate proxies (Trouet et al., 2009). This shift indicates weaker westerly winds during the LIA, reducing convection in the Labrador Sea and therefore decreasing AMOC strength (Dickson et al., 1996). However, not all of the climate variability seen in the Northern Hemisphere during this period can be explained by changes in the NAO mode alone (Palastanga et al., 2011).

Work by Moffa-Sanchez et al. (2014) suggests that a reduction in the AMOC due to freshwater influx may also be partially responsible for the climate transition between the MCA and the LIA. The authors looked at oxygen isotope signatures and assemblages of several different planktonic species in a sediment core from the eastern Labrador Sea. This oxygen isotope record revealed decreased SSTs of 1.5-2.5°C in the Labrador Sea around the start of the LIA. This decrease in SSTs, along with the changes in planktonic species, indicates an increase in the flux of cold and fresh Arctic Waters into the Labrador Sea at the time of the MCA-LIA transition, possibly due to changes in solar minima (Steinhilber et al., 2009) and/or volcanic aerosols (Gao et al., 2007). Fresher conditions would have led to less dense waters and thus less convection in the Labrador Sea, reducing the formation of Labrador Sea Water. This reduction in the rate of deep water formation would have caused a weakening of the AMOC, thus amplifying the cooling in the North Atlantic.

Weakening of the AMOC during the LIA is also evident in the oxygen isotopic signatures of foraminifera in sediment cores from the Florida Straights, which show reduced cross-current density gradients and vertical shear, as well as a decrease in volume transport, during this time period (Lund et al., 2006)(Figure 1.2C). This change in the strength of the AMOC during the LIA compared to the MCA would reasonably have contributed to the cooler climate seen in the Northern Hemisphere during the LIA due to the reduction in northward heat transport. A record of ΔR from ^{14}C isotopes measured in *Arctica islandica* shells off the northern coast of Iceland also indicates reduced AMOC during the LIA (Wanamaker et al., 2012).

Variability in AMOC circulation during this time period was also observed, although not published, by Lloyd Keigwin in a sediment core from near Bermuda (Denton and Broecker, 2008). Keigwin found that ^{14}C measurements in benthic foraminifera indicated the presence of depleted Antarctic Bottom Water during the MCA but not during the LIA. While these data could be interpreted as indicating an increase in strength of the AMOC, it is also possible that North Atlantic Deep Water formation was reduced during the LIA but that the deep water that did form was denser than in the MCA.

Additionally, Denton and Broecker (2008) found a strong correlation between sea ice extent, which the authors took to be an indication of strength of AMOC, to glacial extent in the Northern Hemisphere during the MCA and LIA, again suggesting circulation in the North Atlantic played a large role in Northern Hemisphere climate during this time period. A reconstruction of the AMO also indicates a more negative mode during the LIA when compared to the MCA (Mann et al., 2009), possibly indicative of a shift in AMOC strength.

Conversely, a recent reconstruction of the AMOC over the last millennium suggests no significant change in AMOC strength between the MCA and the LIA (Figure 1.2; Rahmstorf et al., 2015). This reconstruction is based on multiple proxy records and has higher resolution than previous AMOC reconstructions (data are decadally smoothed). However, most of the proxies used are terrestrial based due to the scarcity of marine proxies, especially those with high resolution.

From the above review, it is clear that significant research has been done on past climatic changes in the late Holocene. However, imprecise dating of climate proxies and lack of high resolution marine proxies often hinders a complete comprehension of the timing of climate events in the North Atlantic region along with the identification of drivers for these events. Therefore, more high resolution, absolutely dated marine records are needed in the North Atlantic in order to fully understand the natural variability and climatic drivers in this system. I present one such record for the Gulf of Maine in this thesis.

1.2 The Gulf of Maine

The Gulf of Maine offers a potentially ideal location for reconstructing high resolution North Atlantic climate. Situated on the east coast of North America, the water masses and temperatures of the Gulf of Maine are affected by two of the most prominent ocean current systems in the North Atlantic: the Labrador Current and the Gulf Stream (Figure 1.3). These two current systems influence the water masses transported into the Gulf of Maine and therefore also influence Gulf of Maine

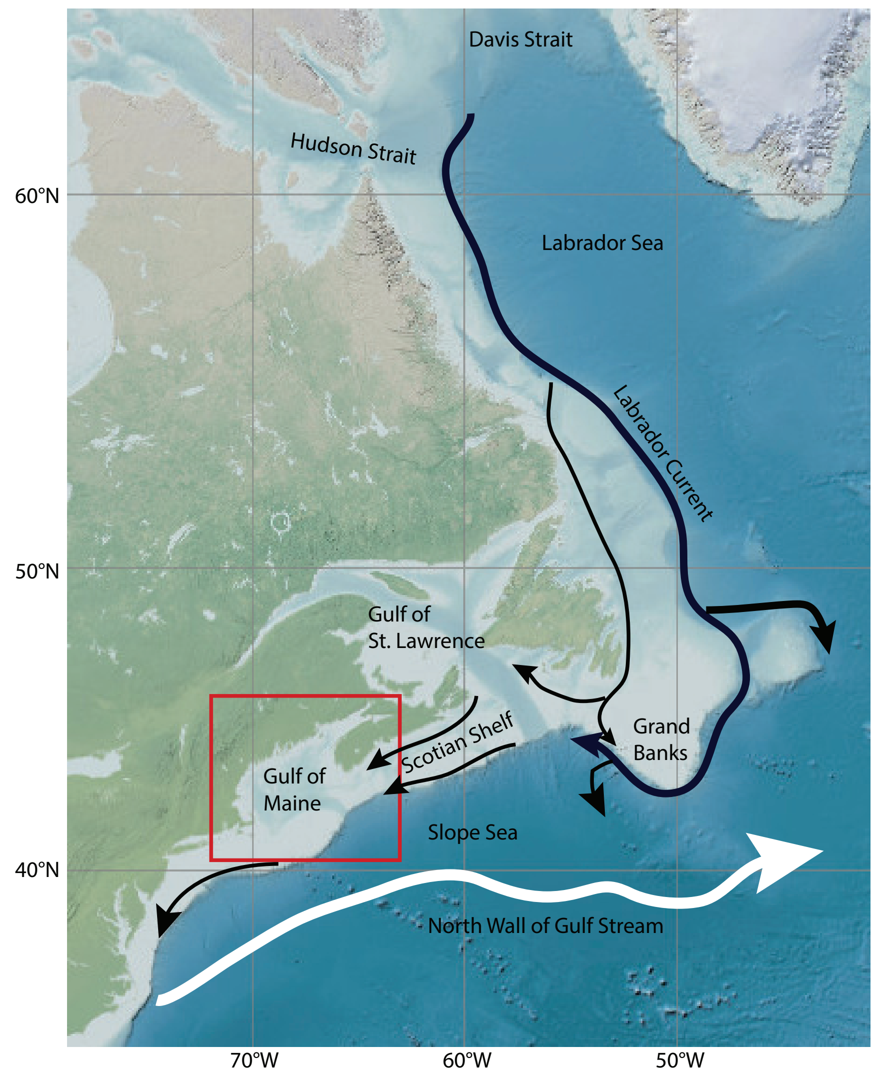

Figure 1.3. Map of the major currents in the western North Atlantic. Currents shown include the Gulf Stream (white arrow) and the Labrador Current (black arrows). Current locations and orientations after Chapman and Beardsley (1989) and Loder et al. (1998). Map modified from (Townsend et al., 2010). Width of arrows indicates the approximate relative strength of currents. The red box marks the location of the Gulf of Maine and of Figure 1.4. Map modified from the NOAA National Geophysical Data Center (maps.ngdc.noaa.gov/viewers/fishmaps).

water temperatures. Larger North Atlantic climate drivers, such as the NAO and the AMOC, influence the strength and position of these current systems so that the proportion of water masses, and the resultant seawater temperatures, that enter the Gulf of Maine is affected by North Atlantic climate dynamics. Reconstructions of this temperature can suggest variability of the broader North Atlantic climate. I present one such reconstruction in this thesis. A review of current Gulf of Maine hydrography, which plays a critical role in the climate of the Gulf of Maine, follows.

1.2.1 Gulf of Maine hydrography

As stated above, the Gulf of Maine waters are affected by two major current systems in the North Atlantic. The Gulf Stream brings warm waters up from the tropics. It follows the general coastline of North America until it reaches Cape Hatteras, where it turns offshore to deeper waters. While Gulf Stream waters are generally not seen in the Gulf of Maine, some warm core rings that have broken off from the Gulf Stream have been observed near the entrance to the Gulf of Maine (Houghton and Fairbanks, 2001). The Gulf Stream does affect the properties of water masses entering the Gulf of Maine, as described below. The other major current system affecting Gulf of Maine waters is the Labrador Current. At over 5000 kilometers long, the Labrador Current is one of the longest coastal currents in the world (Chapman and Beardsley, 1989). The Labrador Current is a buoyancy-driven current that brings waters from the Labrador Sea down the coast of North America. The Labrador Sea is composed of Arctic waters that flow in from Baffin Bay via the Davis Straight, Hudson Bay via the Hudson Straight and via the East and West Greenland currents. While some of the current turns east at the Grand Banks of Newfoundland, the rest turns southwestward along Newfoundland, influencing waters in the Gulf of St. Lawrence and bringing slope waters to the mouth of the Gulf of Maine (Figure 1.3).

The Gulf of Maine is fed by three major water masses that flow in both at depth, through the Northeast Channel, and at the surface from the Scotian Shelf, around Cape Sable (Bigelow, 1927). The deeper water that flows through the Northeast Channel consists of a mixture of Warm Slope Water (WSW) and Labrador Slope Water (LSW) (Gatien, 1976; Ramp et al., 1985; Smith et al., 2001). Both water masses exist in what is termed the Slope Sea, which is an area of the Atlantic between Cape Hatteras and the Grand Banks that is bordered by the continental shelf to the north and the Gulf Stream to the south (Figure 1.3; Csanady and Hamilton, 1988). WSW is found adjacent to the Gulf Stream between 0 and 400 meters depth and is warmer, saltier and higher in nutrients than LSW (Gatien, 1976; Townsend and Ellis, 2010). WSW consists of a mixture of Gulf Stream Water, North Atlantic Central Water and local shelf waters. LSW is generally considered the slope water carried to the southwest by the outer Labrador Current after it has branched off from the inner portion of the Labrador Current, which flows into the Gulf of St. Lawrence. In the Slope Sea, it is found at greater depths and to the north of WSW and shelf water (Gatien, 1976). WSW and LSW enter the Gulf of Maine in varying proportions, dependent on a variety of factors that will be discussed below.

The third primary water mass influencing the composition of Gulf of Maine waters is Scotian Shelf Water (SSW). SSW flows around Cape Sable, Nova Scotia via the Nova Scotian current and into the Gulf of Maine as near-surface waters (Smith, 1983, 1989). SSW is relatively cold and fresh (e.g. Pettigrew et al., 1998) and is comprised of shelf waters from Newfoundland and Labrador as well as waters originating from the Gulf of St. Lawrence (Houghton and Fairbanks, 2001).

Once inside the Gulf of Maine, the deep slope waters mix with surface SSW via various physical processes, including upwelling, tidal mixing and winter convective overturning. An intermediate water layer forms on a seasonal basis when surface waters cooled by winter temperatures experience convective sinking and mixing and are trapped in a layer between 50 and 100 meters as the Gulf of Maine stratifies during the warmer summer months (Hopkins and Garfield, 1979).

The dense slope waters that enter the Gulf of Maine flow into three main basins: Georges Basin in the south, Jordan Basin in the north and Wilkinson basin in the west. These dense waters create baroclinic, cyclonic circulation throughout the Gulf of Maine, with the Gulf of Maine Coastal Current (GMCC) being the primary outer current system. Density gradients in the Gulf of Maine also set up smaller cyclonic gyres around Jordan and Georges basin (Figure 1.4; Beardsley et al., 1997; Bigelow, 1927; Brooks, 1985; Pettigrew et al., 2005; Pettigrew and Hetland, 1995).

There are two major branches of the GMCC, the Eastern Maine Coastal Current (EMCC) and the Western Maine Coastal Current (WMCC) (Pettigrew et al., 2005). The EMCC flows from the south side of the Scotian Shelf, into the Bay of Fundy and southward to Penobscot Bay, where a portion of it turns offshore into the Jordan Basin gyre. The rest of the EMCC continues southward, where it joins the WMCC and flows past Seguin Island, where the shells for the research presented in this thesis were collected, through Casco Bay, down to Cape Cod and Georges Bank. The proportion of the EMCC that combines with the WMCC varies from year to year. Some years, most of the EMCC has been shown to continue southward past Penobscot Bay without recirculating in Jordan basin. Other years, very little if any of the EMCC combines with the WMCC. The reasons for this variation in current flow are not entirely clear (Pettigrew et al., 2005).

1.2.2 Influences on Gulf of Maine water properties

Gulf of Maine seawater temperatures are strongly influenced by the intensity and relative position of the Labrador Current and the Gulf Stream, which dictate the proportion of cold, fresh LSW to warm, salty WSW that enter the Gulf of Maine (Colton Jr., 1968; Petrie and Drinkwater, 1993; Worthington, 1964). Several authors

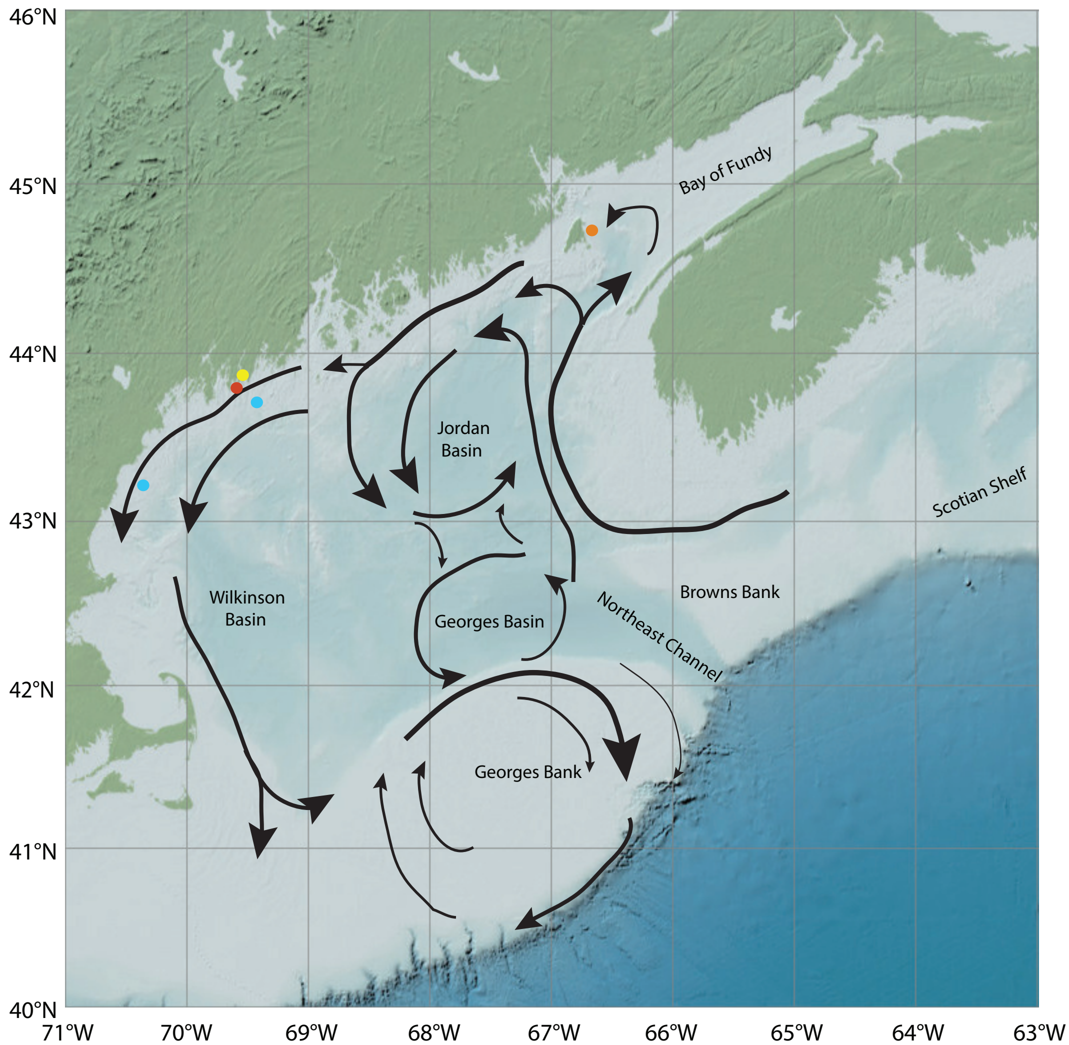

Figure 1.4. Map of the Gulf of Maine. Major geographic features are labeled. Major surface currents are shown by the arrows with the width of the arrow indicating the approximate relative strength of the current. Modified from Pettigrew et al. (2005). The yellow dot marks the location of the Boothbay Harbor Environmental Monitoring Program station. The orange dot marks the location of the Canadian Prince 5 station. The blue dots mark the location of the Northeastern Regional Association of Coastal and Ocean Observing Systems (NERACOOS) buoys referred to in this thesis (B01 to the west of E01). The red dot marks the location off of Seguin Island where *Arctica islanica* shells were collected for the research presented in this thesis. Map modified from the NOAA National Geophysical Data Center (maps.ngdc.noaa.gov/viewers/fishmaps).

have suggested that the positioning of the Labrador Current and the Gulf Stream in relation to the entrance to the Gulf of Maine is driven by the NAO (Drinkwater et al., 1998; Petrie, 2007). This relationship is thought to be caused by weaker westerly winds, which occur during an NAO negative year and decrease winter heat loss and convection in the Labrador Sea. This reduction in heat loss and convection increases the buoyancy and transport of the Labrador Current (Dickson et al., 1996). Weaker westerly winds also move the north wall of the wind-driven Gulf Stream to the south (Taylor and Stephens, 1998). Therefore, with a lag of approximately two years after an NAO low year, a greater intensity Labrador Current carries an increased flux of LSW to the entrance to the Gulf of Maine while WSW, which exists adjacent to the Gulf Stream, moves farther offshore. A greater proportion of LSW to WSW consequently enters the Gulf of Maine, corresponding to a decrease in Gulf of Maine SSTs (Greene and Pershing, 2001). The correlation between the NAO and Gulf of Maine seawater temperatures appears to be weakening in recent decades, possibly due to increased melting in the Arctic causing increased flow of SSW into the Gulf of Maine, thereby decreasing the influence of slope waters on hydrographic properties (Mountain, 2012; Townsend et al., 2010). An increased inflow of SSW appears to lead to decreased inflow of slope water due to mass balance forces. Additionally, a barotropic pressure gradient develops due to the increased flow of fresher water, which possibly decreases the amount of slope water allowed to flow into the Gulf of Maine (Pettigrew et al., 2011, 2008; Smith et al., 2001, 2012).

In addition to the influence that the NAO seems to have on Gulf of Maine waters, recent modeling and observational studies suggest that variability in AMOC strength may influence Gulf of Maine water properties (Dima and Lohmann, 2010; Joyce and Zhang, 2010; Zhang, 2008). It is intuitive to think that during periods of increased AMOC strength, waters in the Gulf of Maine would be warmer like they are believed to be in much of the rest of the North Atlantic. However, Joyce and Zhang (2010);

Zhang (2008) used ocean observations combined with climate models to show that during periods of increased strength in the AMOC, the Gulf Stream has a more southerly route. Conversely, when there are reductions in AMOC strength, the Gulf Stream's path moves to the north. This correlation indicates that with increased AMOC strength, the warm waters brought up from the tropics by the Gulf Stream are farther offshore, allowing for an increased proportion of LSW to enter the Gulf of Maine compared to WSW. Therefore, Gulf of Maine water temperatures would be expected to have an inverse relationship to the strength of the AMOC.

Unfortunately, the instrumental record in the Gulf of Maine is too short to accurately assess the relationship between the NAO, the AMOC and Gulf of Maine water temperatures. The instrumental record in the Gulf of Maine is only 110 years old and not very reliable, as discussed below. Additionally, the correlation between the NAO and Gulf of Maine water temperatures has changed significantly in the short time that both have been recorded (Mountain, 2012; Townsend et al., 2010). It is unclear whether these changes are due to some fundamental change in the hydrography of the region or are instead suggestive of the weaker than believed relationship between the NAO and Gulf of Maine water temperatures. Clearly, a longer reconstruction of water temperature in the Gulf of Maine is necessary in order to better understand the relationship between North Atlantic climate drivers and Gulf of Maine water properties and therefore better understand North Atlantic climate dynamics in general.

1.2.3 The long-term instrumental record in the Gulf of Maine

As discussed above, the task of identifying major drivers of climate in the Gulf of Maine is made difficult by the lack of long-term, reliable instrumental records. One of the few is the Boothbay Harbor Environmental Monitoring Program Station, which was installed in March 1905 and has been recording SSTs on twice daily

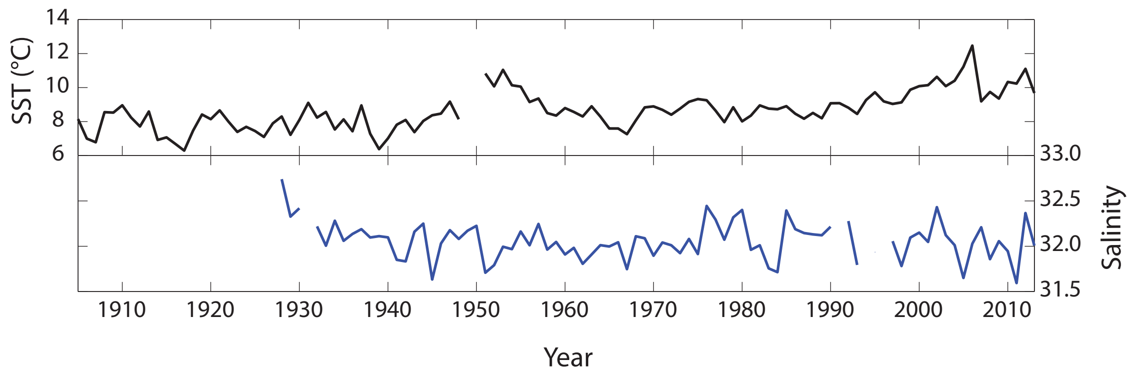

Figure 1.5. Long term instrumental records in the Gulf of Maine. (A) The Boothbay Harbor average annual sea surface temperature (SST) record from the Boothbay Harbor Environmental Monitoring Program Station. (B) The Bay of Fundy average annual salinity record from 50 meters depth at the Canadian Prince 5 station and data collected nearby (i.e. CTD casts and ships of opportunity).

intervals since, except for much of the years 1949-1950 (Figure 1.5). It is one of the longest continuous records of seawater temperatures on the east coast of North America. This station has also been recording temperatures at 8 meters depth since 1989. The Boothbay Harbor station is situated in West Boothbay Harbor at the Department of Marine Resources Fisheries Laboratory (43.844444°, −69.641667°).

Despite its relative longevity, using this record to look at changes in seawater temperatures over the last 110 years is problematic because of changes in sampling method, as noted by Drinkwater and Petrie (2011). Water temperatures at Boothbay Harbor were originally recorded at the surface with a bucket thermometer until 1950 when a fixed thermistor was installed at 1.7 meters depth. Because Boothbay Harbor is highly stratified during the summer, there appear to be much greater seasonal anomalies pre-1950s compared to post-1950s due to this sampling depth difference.

Because the Boothbay Harbor record is the only long-term seawater temperature record in the Gulf of Maine outside of the Bay of Fundy, a description of trends in this record follows. However, it is important to keep in mind the change of sampling method noted above. The Boothbay Harbor station temperature data show anomalously high seawater temperatures in the 1950s, followed by anomalously low seawater temperatures in the 1960s. These latter anomalies were likely due to the influence of the consistently low modes of the NAO during that time period (Drinkwater et al., 1998). Since the 1970s, seawater temperatures have been slowly increasing, with recent positive anomalous seawater temperatures, compared to the 1905-1999 mean, as high as $3 - 4.5$°C seen during late summer, fall and early winter (Fogarty et al., 2007). The record does show recent SSTs as being warmer than any previously recorded at the Boothbay station, even when compared to the anomalously warm temperatures of the 1950s. However, Drinkwater and Petrie (2011) note that since 2001, the temperatures recorded at Boothbay Harbor are significantly warmer than other areas in the Gulf of Maine where instrumental data exists. While the reason for this discrepancy is not clear, it does suggest that perhaps Boothbay Harbor is not representative of the rest of the Gulf of Maine, at least recently.

Temperature and salinity in the Gulf of Maine has been recorded at the Canadian Prince 5 station in the Bay of Fundy (44.946667°, −66.811667°) since 1928. This monitoring station is owned by Fisheries and Oceans Canada and is part of the St. Andrew's Biological Station. Salinity at the Prince 5 station has remained fairly constant, at a value of 32.1 ± 0.22 PSU, in the Gulf of Maine since it was first measured in 1928, with no significant trends present (Figure 1.5; Wanamaker et al., 2008*a*).

More recently, multiple buoys were installed in various locations in the Gulf of Maine during the summer of 2001 as part of the Northeastern Regional Association of Coastal and Ocean Observing Systems (NERACOOS; Figure 3.2). While short in duration, these buoys provide valuable instrumentation of various characteristics of Gulf of Maine waters, including temperature and salinity at various depths (http://gyre.umeoce.maine.edu/buoyhome.php).

Infrared satellite technology has also been recording SSTs in the Gulf of Maine since the 1970s. This data has recently been used to suggest that 2012 was 1-3° warmer than the 1982-2011 average and that the Gulf of Maine has been warming by 0.026°C/yr since 1982 and 0.26°C/yr since 2004, faster than 99% of the global ocean (Mills et al., 2013; Pershing et al., 2014). It is important to keep in mind that these findings have not been published in a peer reviewed journal. In addition, the instrumental records in the Gulf of Maine, summarized above, do not suggest such a significant warming in the Gulf of Maine or that 2012 was a particularly anomalous year (D. Townsend, personal communication).

Therefore, the data provided by the long-term instrumental records in the Gulf of Maine are not adequate for understanding climate dynamics in this region and the broader North Atlantic, both because of the short duration of these records and because some of the records available do not seem to accurately reflect long-term trends or the broader Gulf of Maine.

1.2.4 Previous reconstruction of climate in the Gulf of Maine

Limited work has so far been done on reconstructing Gulf of Maine climate in the late Holocene. Wanamaker et al. (2008*a*) presented carbonate oxygen isotope data ($\delta^{18}O_c$) from four *Arctica islandica* shells (one live-caught and 3 fossil) collected in the Gulf of Maine. These data reveal an increase in $\delta^{18}O_c$ of 0.47‰ over the last 1000 years. This increase likely corresponds to a decrease in seawater temperatures in the Gulf of Maine of approximately 1-2°C (Wanamaker et al., 2008*a*). From this record, Wanamaker et al. (2008*a*) found that 11-18% of water temperature variability from 1950-2003 was a result of NAO variability (2 year lag). While this is a good start to reconstructing climate in the Gulf of Maine, there are several aspects of the study that need to be improved upon before a solid understanding of climate in this region and the broader North Atlantic can hope to be achieved. There are large gaps in the Wanamaker et al. (2008*a*) 1000 year reconstruction: from 1078 ± 78 AD to 1321 ± 45 AD, from 1470 ± 45 to 1864 AD, and from 2003 to present. In addition, the shells used in this study were not crossdated into a chronology and the three fossil shells were dated using radiocarbon methods. Consequently, the $\delta^{18}O_c$ time series presented by Wanamaker et al. (2008*a*) has inherent dating errors associated with it. Therefore, a record that fills in these gaps and reduces dating errors is needed.

1.3 Introduction to the current study

The research presented in this Master of Science thesis is a portion of the work currently being conducted to reconstruct hydrographic variability in the Gulf of Maine using a high resolution proxy in order to contribute to the understanding of the climate system in the North Atlantic and the Gulf of Maine. Below is an introduction to the proxy and techniques used for this reconstruction.

1.3.1 *Arctica islandica* as an ocean climate proxy

While numerous annually resolved, precisely dated proxy records have been developed for the tropical (corals), terrestrial (tree rings) and cryospheric (ice cores) environments, such a proxy was, until recently, lacking for the North Atlantic extratropical region. To fill the need for extratropical marine proxies in the North Atlantic, recent work has looked at the long-lived mollusc *Arctica islandica.* Several precisely dated, annually resolved master chronologies, mostly in the eastern North Atlantic, have been constructed using *A. islandica* shells (Butler et al., 2013; Schöne et al., 2003*a*).

There are many qualities of *A. islandica* that make it an ideal marine climate proxy. These include the fact that its shell grows in annual increments (Jones, 1980; Thompson et al., 1980), allowing climate data obtained from these increments to be annually resolved. These annual increments record the environmental conditions in which they grew, both by variation in the increment widths (Schöne et al., 2003*b*; Wanamaker et al., 2009; Witbaard, 1997) and the preservation of geochemical records (Schöne et al., 2011; Wanamaker et al., 2011, 2008*a*; Witbaard et al., 1994). In particular, *A. islandica* shells precipitate in isotopic equilibrium with the surrounding water and therefore the shells provide valuable isotopic data that can be utilized to look at climate variability (Weidman et al., 1994). Because the width of the annual shell increments is due to external environmental conditions, presumably experienced by all *A. islandica* living in the same area, the pattern of the relative widths of the annual increments in one shell specimen can be matched to the same pattern in another shell specimen. This correlation of increment width patterns amongst specimens allows for the building of precisely dated chronologies by taking a shell that was caught live and matching the pattern of the increments to a fossil shell, thereby absolutely dating the fossil shell and extending the chronology back in time, one shell at a time. This dating technique is called crossdating and originated in the field of dendrochronology.

In addition to the environmental signals that *A. islandica* preserves in its shell, this species is particularly useful for climate reconstructions due to the fact that it is the longest-lived, non-colonial species in the world, with a maximum lifespan of 375-507 years (Butler et al., 2013; Schöne et al., 2005; Wanamaker et al., 2008*b*). Consequently, a single specimen has the potential to provide many hundreds of years of climate data. In addition, the habitat of *A. islandica* is expansive, covering much of the North Atlantic and ranging from shallow waters down to 500 meters in depth (Figure 1.6; Dahlgren et al., 2000; Nicol, 1951). This large range of habitat

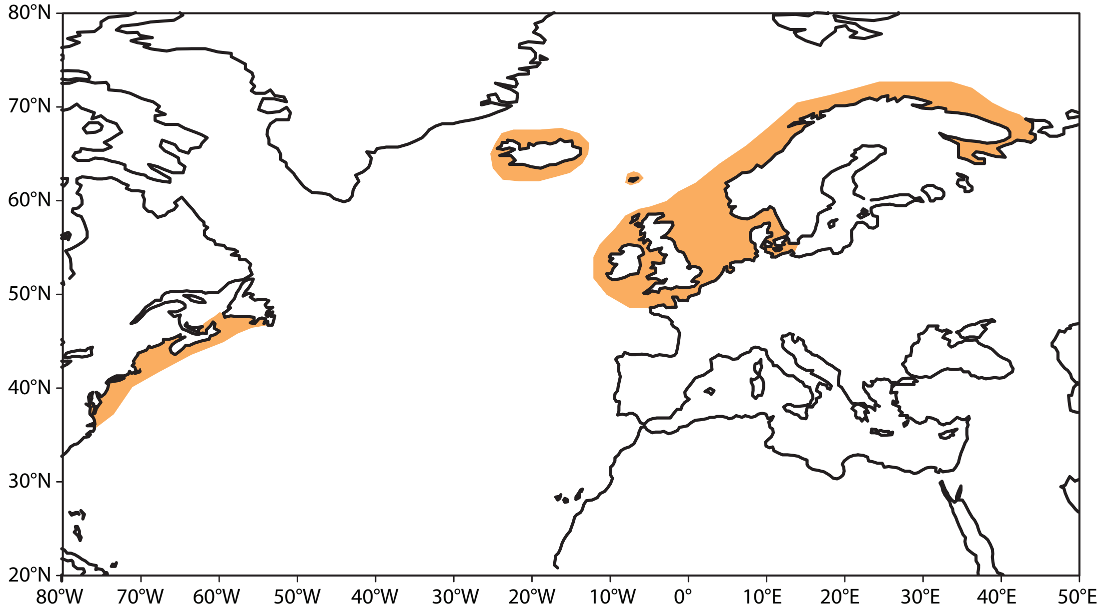

Figure 1.6. Map of the modern-day distribution of *Arctica islandica*. Distribution depicted by orange shading and based on Dahlgren et al. (2000).

provides the opportunity to develop proxy records using *A. islandica* shells for a large portion of the climatically important extratropical North Atlantic. Therefore, *A. islandica* provide an ideal proxy for developing high-resolution, precisely dated climate records in the North Atlantic.

1.3.2 Reconstructing water temperatures using *A. islandica*

As mentioned in the previous section, one of the characteristics that make *A. islandica* shells such a valuable climate proxy record is the fact that they precipitate their shells in isotopic equilibrium with the surrounding seawater. The term oxygen isotopic equilibrium refers to the fact that the ratio of heavy (^{18}O) to light (^{16}O) oxygen isotopes found in *A. islandica* shells is only determined by the seawater temperature and the ratio of heavy to light oxygen isotopes in the seawater during the time that the organism is growing its shell. That is to say that no internal biological factors, known as vital effects, influence the oxygen isotopic composition of *A. islandica* shells. As ions are removed from seawater during the precipitation of an *A. islandica*'s aragonitic shell, ^{18}O is removed preferentially over ^{16}O (McCrea, 1950) so that the ratio of heavy to light isotopes is greater in the shell than in the seawater. As the temperature of the environment in which the reaction is occurring increases, the difference in the ratio of ^{18}O to ^{16}O between the shell and seawater decreases as the "preference" of the reaction for the heavier over the lighter isotope decreases.

The fact that *A. islandica* shells precipitate in isotopic equilibrium with seawater allows for the reconstruction of the seawater temperature at the time that the shell formed from the oxygen isotopic measurements of that shell, assuming that the oxygen isotopic signature of the seawater is known. This relationship between oxygen isotopes from *A. islandica* shells and seawater temperatures was demonstrated by Weidman et al. (1994), who investigated the oxygen isotopic composition of *A. islandica* shells collected on Nantucket Shoals, off of the coast of North America (Figure 1.7). By comparing the oxygen isotopic composition of these shells to nearby instrumental records, the authors were able to show that seawater temperatures can be derived from oxygen isotopic ratios of *A. islandica* shells using the equation first developed for molluscs by Grossman and Ku (1986) and later modified to adjust for differences in isotopic standards:

$$T(^{\circ}C) = 20.60 - 4.34(\delta^{18}O_c - (\delta^{18}O_w - 0.27)) \tag{1.1}$$

δ (delta) notation is the standard method for reporting isotopic measurements and is defined as follows:

$$\delta^{18}O = \frac{\frac{^{18}O}{^{16}O}_{sample} - \frac{^{18}O}{^{16}O}_{standard}}{\frac{^{18}O}{^{16}O}_{standard}} \times 100 \tag{1.2}$$

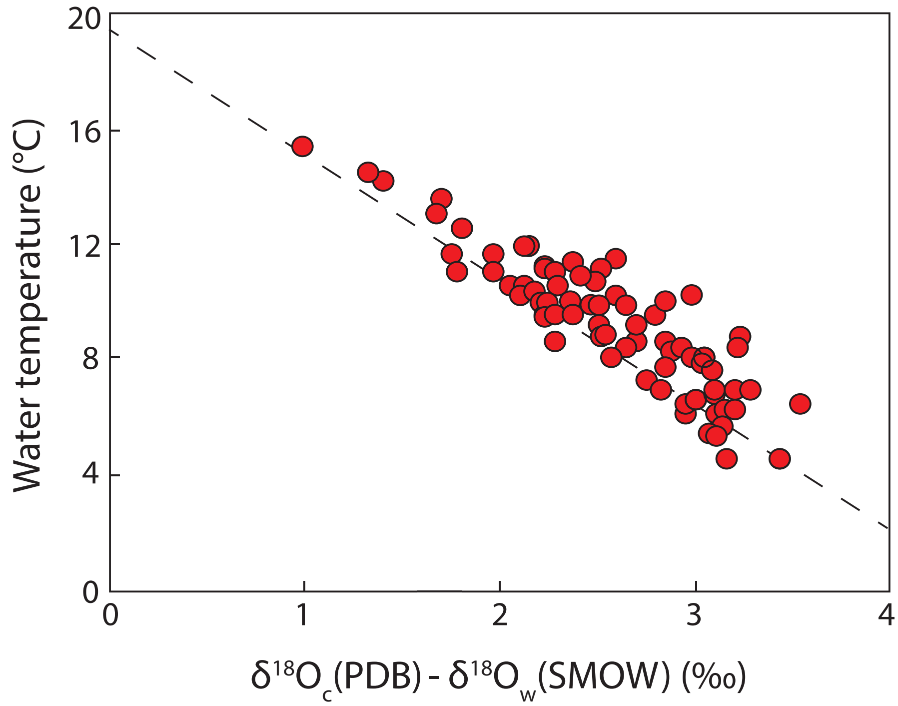

Figure 1.7. Plot showing temperature dependence of *Arctica islandica* shell $\delta^{18}O_c$. The dashed line is the modified equation from Grossman and Ku (1986) for the relationship between temperature and oxygen isotopes measured in molluscs (equation 1.1). The red dots are data from Weidman et al. (1994) using oxygen isotope data measured in *A. islandica* shells. Subscripts c and w indicate oxygen isotopes measured in carbonate and water respectively.

The international standard used today is Vienna PeeDee Belemnite (VPDB) for carbonates and Vienna Standard Mean Ocean Water (VSMOW) for water. The subscripts c and w in equation 1.1 denote carbonate and water respectively.

It is clear from equation 1.1 that the oxygen isotopic signature of the water is needed in order to calculate seawater temperatures from the oxygen isotopic measurements in carbonate. Unfortunately, this value is rarely available. However, the oxygen isotopic composition of seawater has a positive, linear relationship with salinity of seawater as both are conservative seawater properties that are affected by the difference in evaporation and precipitation in the area in which the water mass formed. The relationship between $\delta^{18}O_w$ and salinity varies by location. Therefore, records of salinity near an area where the sampled *A. islandica* shells were collected can be used to determine what the oxygen isotopic signature of the seawater was when the shell was precipitated if the $\delta^{18}O_w$-salinity relationship has been determined for the collection area. Additionally, studies that seek to define this relationship in a given region can also assess the origin and mixing of water masses in the region as both $\delta^{18}O_w$ and salinity are conservative properties of water and therefore act as water mass tracers.

1.4 Thesis overview

With the research conducted for this Master of Science thesis, I seek to improve the understanding of natural variability, climatic dynamics and hydrographic changes in the Gulf of Maine and consequently the broader North Atlantic region in the late Holocene through the analysis of oxygen isotopes in *A. islandica* shells. Before reconstructions of seawater temperatures can be derived from any oxygen isotope data collected, a better understanding of the relationship between oxygen isotopes and salinity in the coastal Gulf of Maine is needed. In Chapter 2 of this thesis, I present $\delta^{18}O_w$ and salinity values as well as the resultant $\delta^{18}O_w$-salinity mixing lines for water samples collected in the coastal waters of the Gulf of Maine over the past several years. I also use these data to draw conclusions about the water masses that compose coastal waters in the Gulf of Maine and how these compositions vary on seasonal and annual time scales.

In Chapter 3 of this thesis, I present oxygen isotope ratios measured in *A. islandica* shells cross-dated into a multi-specimen growth series that is precisely dated from 1683-2009. The data I present in this chapter span the time period between 1695 and 1915 and enable conclusions about hydrographic natural variability and climate drivers within the Gulf of Maine as well as offer potential reconstructions for broader North Atlantic climate drivers.

In Chapter 4, I offer conclusions about past, present and future climate in the Gulf of Maine and the North Atlantic that can be drawn from the research I present in this thesis. Additionally, I outline future work that is necessary to improve our understanding of climate and climate drivers in the Gulf of Maine and the broader North Atlantic.

Chapter 2
SPATIAL AND TEMPORAL VARIABILITY IN THE $\delta^{18}O_W$ AND SALINITY COMPOSITIONS OF GULF OF MAINE SURFACE COASTAL WATERS

2.1 Chapter abstract

Hydrographic variability and dynamics in the Gulf of Maine are examined through the investigation of $\delta^{18}O_w$ and salinity properties of coastal surface waters. Two different data sets are presented, one consisting of water samples collected from 2003-2013 in coastal waters primarily in the western Gulf of Maine and the other collected monthly from April-December of 2014 in coastal waters primarily in the eastern Gulf of Maine. These coastal water samples fall on a mixing line between Maine River Water (MRW) and Scotian Shelf Water (SSW) and indicate very little if any mixing of slope waters. Differences in end members between the two data sets likely indicate differences in freshwater composition between the western and eastern Gulf of Maine as well as year to year variability in SSW composition.

The seasonal variability in water samples collected during 2014 indicates the strong influence of river runoff on coastal Gulf of Maine surface water properties. The dominant trends of low $\delta^{18}O_w$ and salinity values during spring and early winter and higher values during summer and fall follow closely both the seasonal trends in $\delta^{18}O_w$ of rivers as well as those in river discharge. Changes in river discharge seem to dominate coastal water property variability, as indicated by both trends in salinity, which vary with $\delta^{18}O_w$, as well as comparisons in isotopic composition across sampling locations.

2.2 Introduction

The location of the Gulf of Maine, a semi-enclosed sea on the eastern continental shelf of North America, makes the area a potentially valuable indicator of past hydrographic variability in the North Atlantic. Before hydrographic changes in the broader region can be interpreted from hydrographic changes seen in the Gulf of Maine, both in the past and in the present, Gulf of Maine hydrographic dynamics must be comprehensively understood through an assessment of the composition and origin of water masses contributing to Gulf of Maine waters. These characteristics of Gulf of Maine waters have been described in detail by numerous authors (Bigelow, 1927; Brown and Irish, 1993; Chapman et al., 1986; Chapman and Beardsley, 1989; Fairbanks, 1982; Gatien, 1976; Houghton and Fairbanks, 2001; Smith, 1983; Smith et al., 2001). Here, I focus on the use of oxygen isotopes and salinity in determining the hydrography of the Gulf of Maine.

2.2.1 δ^{18}O and salinity as conservative water mass tracers

The oxygen isotopic composition of a water mass ($\delta^{18}O_w$) is related to the latitudinal origin of that water. Water vapor parcels and therefore the resultant precipitation becomes progressively more depleted (the ratio of heavy to light oxygen isotopes decreases) with increasing latitude as heavy oxygen isotopes are preferentially removed from the water vapor parcel via precipitation as that parcel condenses with decreasing temperatures. Therefore, the freshwater that feeds ocean water masses, via both direct precipitation and river runoff, is progressively more depleted with increasing latitude (Dansgaard, 1964). Consequently, ocean water masses originating from different latitudes will have different oxygen isotopic signatures. Because $\delta^{18}O_w$ is not changed by biological processes during transport, $\delta^{18}O_w$ is considered a conservative property of water masses.

$\delta^{18}O_w$ has a positive linear relationship with salinity, which is another conservative property of water masses. This relationship (referred to as a "mixing line" in this paper due to its indication of the mixing of two or more water masses) exists because both $\delta^{18}O_w$ and salinity are directly affected by the amount of freshwater input (both via precipitation and river runoff) and evaporation occurring in a given area. The greater the difference between evaporation and freshwater input, the more saline a water body will be because salt ions do not evaporate with water molecules. At the same time, the greater the difference between evaporation and precipitation, the more isotopically enriched the remaining water reservoir will become as evaporation preferentially favors lighter oxygen isotopes (Gat, 1996). This relationship between salinity and $\delta^{18}O_w$ can therefore be used to determine water mass origin and mixing in any given region, such as the Gulf of Maine.

There have been numerous studies that use oxygen isotopes and salinity as conservative water mass tracers in and around the Gulf of Maine. I will first review the work that has been done on identifying oxygen isotopes and salinity signatures of water masses that flow into the Gulf of Maine before discussing specific oxygen isotope studies in the region.

2.2.2 Regional water mass composition

The Gulf of Maine is fed by several different water masses which have been described by their temperature, oxygen isotope and salinity signatures (Table 2.1). The general origin of these water masses is shown in Figure 2.1. Deep waters in the Gulf of Maine have been shown by numerous authors to be composed of Labrador Slope Water (LSW) and Warm Slope Water (WSW). LSW is generally considered water that is transported by the southwestward flowing branch of the Labrador Current after it has split to divert some water into the Gulf of St. Lawrence (Chapman and Beardsley, 1989). LSW was first characterized by Gatien (1976), who described

Water Mass	Temperature (°C)	$\delta^{18}O_w$ (‰)	Salinity	Source
Warm Slope Water (WSW)	10	0.4	35.2	Houghton and Fairbanks, 2001
	11.11 (potential)	**0.36**	**35.16**	Khatiwala et al., 1999
Labrador Slope Water (LSW)	6	0.22	34.9	Houghton and Fairbanks, 2001
	3.28 (potential)	**0.22**	**34.804**	Khatiwala et al., 1999
Scotian Shelf Water (SSW)		**-1.09**	**32.35**	Chapman et al., 1986
		-1.4	32	Smith et al., 2001
Labrador Shelf Water (LShW)	0	-1.62	32.6	Houghton and Fairbanks, 2001
St. Lawrence Estuary Water (SLEW)		-2.45	29.5	Houghton and Fairbanks, 2001
St. Lawrence River Water (SLRW)		-10.3	0	Khatiwala et al., 1999
Arctic River Water (ARW)		-21	0	Khatiwala et al., 1999
Maine River Water (MRW)		-10.89	0	Fairbanks1982
Gulf Stream Water		1.15	36.2	Fairbanks, 1982
	16	1.05	35.95	Houghton and Fairbanks, 2001

Table 2.1. Properties of water masses composing Gulf of Maine waters. Bolded numbers are those chosen for figures and discussion in this paper. These water mass property definitions were largely determined from the end members of salinity and $\delta^{18}O_w$ mixing lines derived from water samples collected on research cruises during the 1980s and 1990s. It is important to note that not all of these definitions take into account annual and monthly changes to the water masses but are meant to give rough estimates.

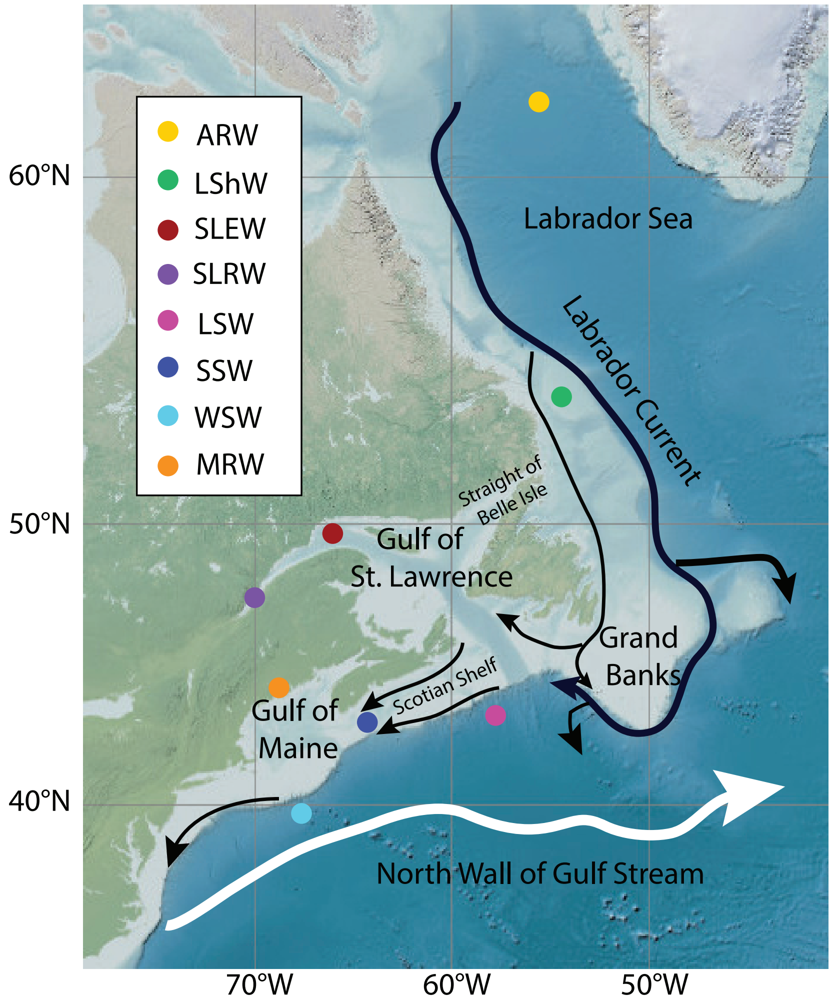

Figure 2.1. Map of the general area of origin of water masses believed to contribute to the compositions of Gulf of Maine waters. These water masses include Arctic River Water (ARW; Khatiwala et al., 1999), Labrador Shelf Water (LShW; Khatiwala et al., 1999), St. Lawrence Estuary Water (SLEW; Houghton and Fairbanks, 2001), St. Lawrence River Water (SLRW; Khatiwala et al., 1999), Labrador Slope Water (LSW; Chapman and Beardsley, 1989), Scotian Shelf Water (SSW; Chapman et al., 1986; Smith, 1983), Warm slope Water (WSW; Gatien, 1976), Maine River Water (MRW; Fairbanks, 1982). The justification for choosing the location of origin for these water masses is described in the text. Major western North Atlantic Currents are also shown: the Gulf Stream (white arrow) and the Labrador Current (black arrows), after Chapman and Beardsley (1989) and Loder et al. (1998) and modified from Townsend et al. (2010). Width of arrows indicates the approximate relative strength of currents. Map modified from the NOAA National Geophysical Data Center (maps.ngdc.noaa.gov/viewers/fishmaps).

LSW as poorly-mixed, westward flowing water that could be found at depths below 100 meters. Khatiwala et al. (1999), whose water mass definitions largely come from data collected on research cruises in June and November of 1995, define LSW as the highest salinity water on the Labrador Slope, which can be found between 400 and 500 meters depth.

WSW was first described by Gatien (1976) as water found at 0-400 meters depths adjacent to the Gulf Stream. WSW is the primary slope water mass south of Nova Scotia and is defined by Khatiwala et al. (1999) as the warmest slope water in the Gulf of Maine. WSW is more nutrient rich compared to LSW (Townsend and Ellis, 2010). Both slope waters enter the Gulf of Maine via the Northeast Channel.

Scotian Shelf Water (SSW) is the shallow water that enters the Gulf of Maine from the Scotian Shelf over Cape Sable (Chapman et al., 1986; Smith, 1983). By investigating the $\delta^{18}O_w$-salinity relationship of waters on the Scotian Shelf, Khatiwala et al. (1999) determined that SSW was composed of LSW, Labrador Shelf Water (LShW) and St. Lawrence River Water (SLRW). Khatiwala et al. (1999) defined LShW as the shallow waters on the Labrador Shelf just north of the Straight of Belle Isle, where water carried by the coastal branch of the Labrador Current flows into the Gulf of St. Lawrence. Houghton and Fairbanks (2001)'s definition of Labrador Shelf Water is slightly saltier and more depleted as samples used for their definition of the water mass were collected in the Straight of Belle Isle. SLRW is defined by Khatiwala et al. (1999) to be the freshwater end member of St. Lawrence Estuarine Water, which is consistent with the $\delta^{18}O_w$ of freshwater entering the Gulf of St. Lawrence from the St. Lawrence River, by far the largest river that flows into the Gulf, as defined by Tan and Strain (1980). Houghton and Fairbanks (2001) define the freshwater source in the Gulf of St. Lawrence as St. Lawrence Estuary Water (SLEW), which they characterize by the lowest salinity water found in the Gulf of St. Lawrence (Table 2.1).

Research on the oxygen isotopic composition of water masses in the Gulf of Maine and surrounding regions has elicited some debate as to the source of the fresh water end member of Gulf of Maine waters. Most authors agree that the majority of the freshwater in the Gulf of Maine originates in locations north of this region. Loder et al. (1998) estimated an average freshwater flux (compared to a salinity of 34.8) through the Northeast Channel of 13,000 m^3s^{-1} compared to a river flux input into the Gulf of Maine of 3,000 m^3s^{-1}, indicating that rivers that flow into the Gulf of Maine only contribute 18% of the freshwater found in the Gulf of Maine (Smith et al., 2001).

The northern most possible source of freshwater to the Gulf of Maine is considered to be freshwater flowing out of the Labrador Sea, although there is some question as to whether this freshwater has a significant contribution to Gulf of Maine waters. Khatiwala et al. (1999) defined this depleted end member as Arctic River Water (ARW). The δ^{18}O value of ARW (Table 2.1) was determined based on several different authors measurements of the oxygen isotopic composition of freshwater sources to the Labrador Sea, which are dominated by freshwater input from the Arctic (Aagaard and Carmack, 1989; Bedard et al., 1981; Lazier and Wright, 1993; Loder et al., 1998; Östlund and Hut, 1984; Schlosser et al., 1994; Tan and Strain, 1980, 1996).

While Fairbanks (1982), Chapman et al. (1986), and Chapman and Beardsley (1989) all inferred the freshwater end members ($\delta^{18}O_w$ of $-21‰$) of mixing lines derived from areas in and around the Gulf of Maine to indicate a freshwater source of ARW, Khatiwala et al. (1999) and Houghton and Fairbanks (2001) show that this freshwater end-member is in fact the result of mixing between SLRW and LShW. The mixing of these two water masses results in this low $\delta^{18}O_w$ end member value because of an increase in salinity in LShW due to sea-ice formation, which does not change the isotopic composition of the water. The authors used $\delta^{18}O_w$-salinity mixing lines to determine that SLRW made up 48% of the freshwater (compared to a salinity of 34.8) entering the Gulf of Maine via the Northeast Channel during the time period studied, with the remaining freshwater contributed by LShW. This percentage was determined because water samples fell along a mixing line that indicated a mixture of 5.6% SLRW and 94.4% LShW. The freshwater content of LShW can be determined by using its average salinity of 32.6 in the following equation:

$$\frac{34.8 - 32.6}{34.8} \times 100 = 6.3\% \tag{2.1}$$

The percentage of freshwater contributed by SLRW can then be calculated using the freshwater content of LShW and the percentages of SLRW and LShW found in Gulf of Maine waters:

$$\frac{5.6}{5.6 + (0.063 \times 94.4)} \times 100 = 48\% \tag{2.2}$$

2.2.3 The $\delta^{18}O_w$ and salinity signatures of Gulf of Maine waters

Several studies have looked at the salinity and $\delta^{18}O_w$ composition of waters in and around the Gulf of Maine in order to gain a better understanding of the specific water masses that make up the Gulf of Maine region. Fairbanks (1982) measured the $\delta^{18}O_w$ composition of water samples collected in the Gulf of Maine and Mid-Atlantic Bight (Figure 2.2A), as well as in the largest rivers that drain into these regions. The St. John, Penobscot, Kennebec and Androscoggin Rivers were all sampled on a monthly basis during 1981. The annual weighted average $\delta^{18}O_w$ of the Kennebec and St. John was measured to be 10.89‰ (Maine River Water - MRW - in Table 2.1). Fairbanks determined that these as well as other rivers in the region were enriched by 2‰ in the summer. Additionally, Fairbanks sampled water at various depths in Wilkinson Basin, in the western Gulf of Maine, in January, May and August of

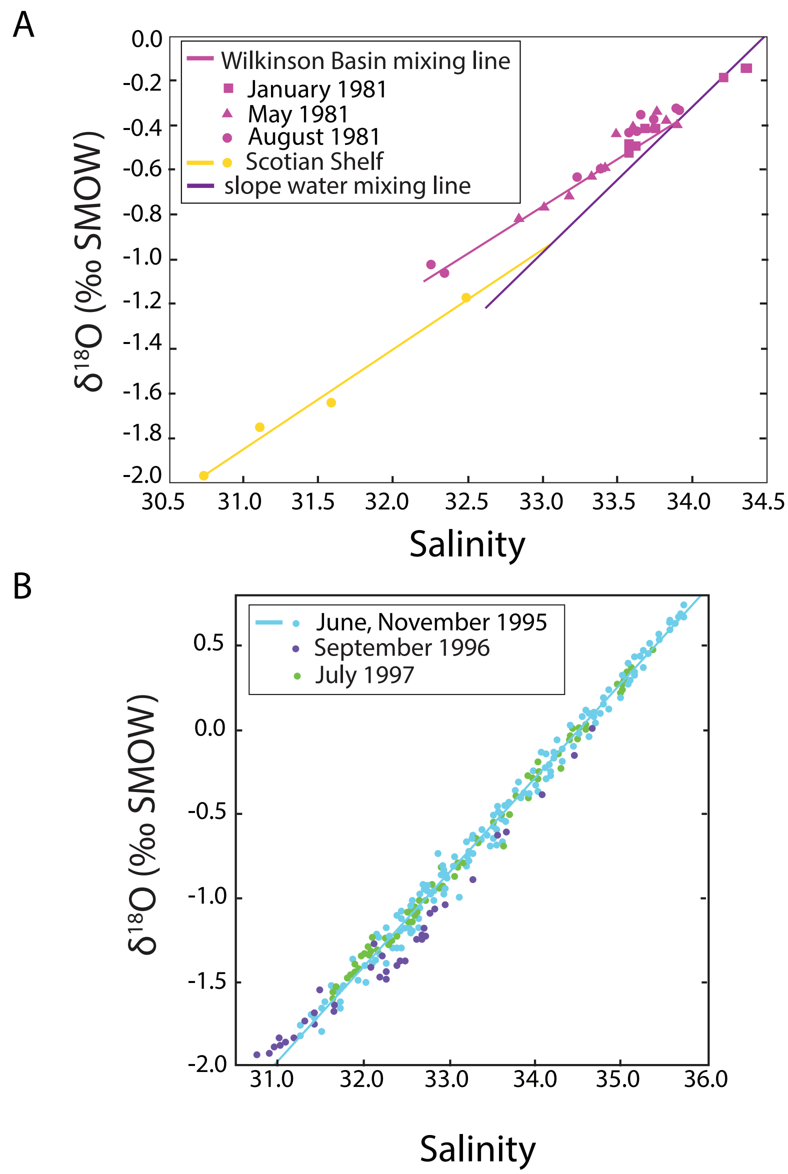

Figure 2.2. Plots of previously published $\delta^{18}O_w$-salinity mixing lines for the Gulf of Maine region. (A) Mixing lines from Fairbanks (1982). The Wilkinson Basin mixing line (equation 2.3) is derived from samples taken from surface and intermediate waters in Wilkinson Basin. Samples collected in January, May and August of 1981 are from various depths in Wilkinson Basin. The Scotian Shelf mixing line and slope water mixing line result in equations 2.4 and 2.5 respectively. (B) The Northeast Channel mixing line from Houghton and Fairbanks (2001). The mixing line derived from samples collected in June and November 1995 results in equation 2.6.

1981. He found that Wilkinson Basin surface and intermediate waters (above 115 meters depth) fall on a two water mass mixing line:

$$\delta^{18}O_w = 0.421S - 14.66 \tag{2.3}$$

This mixing line is very similar to the Scotian Shelf mixing line determined by the author to be

$$\delta^{18}O_w = 0.442S - 15.55 \tag{2.4}$$

and therefore suggests that the near surface and intermediate waters of the Gulf of Maine are primarily fed by SSW, as has been described in several other studies (Hopkins and Garfield, 1979; Smith, 1983).

Slope water, the composition of which Fairbanks determined from samples taken between Nova Scotia and Cape Hatteras, falls on a two water mass mixing line between Gulf Stream waters and fresh water that have an oxygen isotopic value of $-21.6‰$, which the author took to indicate Labrador Sea origin. This results in a mixing line of:

$$\delta^{18}O_w = 0.628S - 21.67 \tag{2.5}$$

Samples of bottom water from Wilkinson Basin fall on this mixing line and suggest that bottom waters in the Gulf of Maine are composed of slope water (WSW and LSW), as separately determined by other authors (e.g. Ramp et al., 1985).

Chapman et al. (1986) looked at oxygen isotope and salinity measurements in transects taken along the Northeast Channel (at the entrance to the Gulf of Maine) and Georges Bank (located on the southwestern border of the Gulf of Maine) as well as transects taken farther south to determine the percentage of various water masses in each of these regions. Consistent with other authors, Chapman et al.

(1986) reported a decrease in the percentage of SSW with depth in the Northeast Channel, indicating the deep inflow of slope water. However, salinity and oxygen isotope data indicate that deep waters in the Northeast Channel were still composed of 20-30% SSW. The authors suggested that this may indicate the mixing of SSW with LSW farther north over the Scotian Shelf, a mixture of water masses that is then transported into the Northeast Channel. The authors found that water around the southern flank of Georges Bank (and thus either exiting the Gulf of Maine or flowing past the Northeast Channel) was 70-80% SSW, indicating that slope waters mix with SSW in the Gulf of Maine. Little to no local river water influence was found on either of the transects taken in the Gulf of Maine, although this is to be expected considering that neither transect was located near the coast.

Similarly, Houghton and Fairbanks (2001) used oxygen isotope measurements to determine the source of waters on Georges Bank and in the Northeast Channel from 1995-1998. The authors obtained their data from various research cruises on Georges Bank, in the Northeast Channel, on the Scotian Shelf, in the Gulf of St. Lawrence, and on the southern Newfoundland Shelf. The authors show that water samples collected in the Northeast Channel fall on a single mixing line with WSW as the saline end member (Figure 2.2B):

$$\delta^{18}O_w = 0.57S - 19.5 \tag{2.6}$$

Smith et al. (2001) used oxygen isotope measurements in water samples collected at various depths on Georges Bank from October 1993 - September 1996 to determine the primary source of freshwater to the region. The authors found large changes in the source of the freshwater from year to year on Georges Bank, with a downward trend of MRW contribution to the freshwater budget on Georges Bank from 1994 to 1997, coincident with a general freshening of the waters in the area. In 1994, MRW contributed 2.4% by volume and 38% of the freshwater (relative to a salinity of 34.8) on Georges Bank. During 1995, MRW contributed 1.4% by volume and 26% of the freshwater on Georges Bank. By 1996-1997, the percentage of freshwater on Georges Bank contributed by MRW was less than 5%. The authors correlated this reduction in the proportion of MRW and general freshening on Georges Bank to anomalously cold winters and large sea ice extent in the northern Labrador Sea and Baffin Bay.

Similar to Smith et al. (2001), Houghton and Fairbanks (2001) found the amount of freshwater on Georges Bank composed of MRW varied significantly from year to year when comparing data collected in 1981 and 1982 and data collected from 1994-1998. MRW made up anywhere between 3.7-55% of the freshwater (compared to a salinity of 34.8) on Georges Bank, as reported by these authors.

While investigations into the oxygen isotopic composition of Gulf of Maine waters have yielded important information on water mass sources and mixing in the Gulf of Maine, there are still large gaps in the research that need to be addressed in order to gain a better understanding of hydrographic variability and dynamics in this climatically important region of the North Atlantic. Specifically, no studies have shown the isotopic composition of coastal, surface waters, how these waters vary from season to season and between regions and what this reveals about hydrographic composition in the Gulf of Maine. In this thesis, I seek to fill that gap by presenting salinity and $\delta^{18}O_w$ data from water samples collected along the coast of the Gulf of Maine over multiple seasons and years.

2.3 Methods

Two sets of water sample data are presented in this thesis. One set is oxygen isotope and salinity data from water samples collected between 2003 and 2013 at

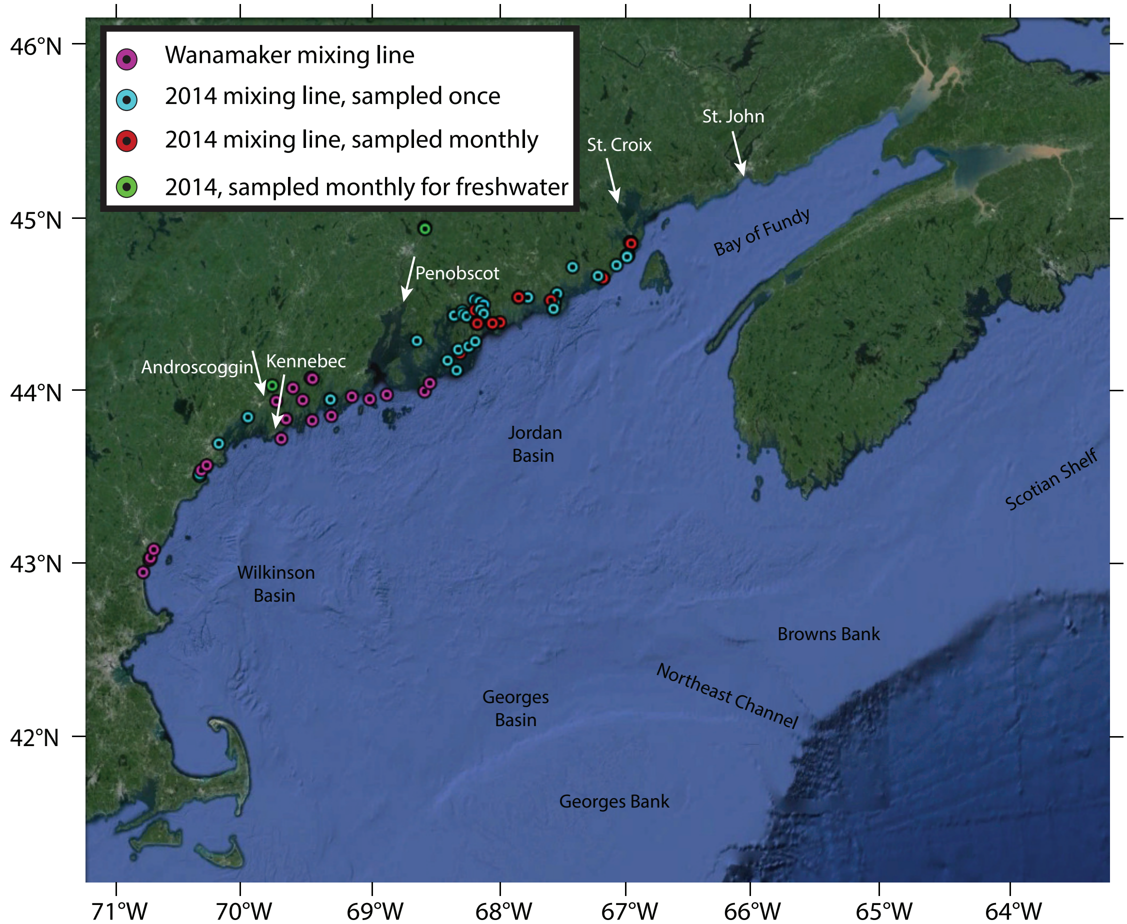

Figure 2.3. Map of water sample collection sites in the Gulf of Maine. The map shows water sample collection sites for the Wanamaker and 2014 coastal mixing lines, as well as freshwater samples collected in 2014. Markers indicate the mixing line for which the location was sampled and how often. White arrows indicate the mouth of five major rivers that empty into the Gulf of Maine. Map modified from Google Earth.

various locations in the Gulf of Maine and termed here the Wanamaker coastal mixing line data set (Figure 2.3, pink markers). Much of this data has been published previously but is compiled here for the first time to form a coastal Gulf of Maine δ^{18}O-salinity mixing line. This data set includes water samples published by Wanamaker et al. (2006), Wanamaker et al. (2007) and Owen et al. (2008), as well as data collected as part of research published by Beirne et al. (2012). The other set of data is comprised of surface water samples collected from April-December 2014 at locations along the coast of Maine (Figure 2.3, red and teal markers) to further improve the coastal Gulf of Maine mixing line as well as to investigate the seasonal variability in hydrographic composition in these areas. This data set is termed the 2014 surface coastal mixing line data set in this paper.

The Wanamaker mixing line data set primarily consists of water samples collected as part of various experiments conducted at the Darling Marine Center in Walpole, Maine. Water samples collected during these experiments were obtained from water pumped into the Darling Marine Center's flowing seawater laboratory from ∼10 meters below mean low tide in the Damariscotta River, an estuarine environment. Additionally, this data set contains data from water samples collected between Seguin Island in the western coastal Gulf of Maine and Isle au Haut in the central coastal Gulf of Maine during July of 2011 and from samples collected along the southern Maine and New Hampshire portion of the Gulf of Maine coast during October of 2013.

Details on data processing of water samples from previously published work are included in those publications. Samples collected during 2010 at the Darling Marine Center and the summer of 2011 (unpublished) were brought to the Stable Isotopes Lab (SIL) at Iowa State University and measured via a Picarro L1102-i Isotopic Liquid Water Analyzer with an attached autosampler. OH-1, OH-2 and OH-3 (only for summer 2011 samples) were used as reference standards. Samples were injected six times, with only the last 4 injections being used to determine the isotopic value of the sample in order to avoid memory effects. The combined uncertainty (analytical and average correction factor) was ±0.15‰ (for 2010 samples) and ±0.04‰ (for 2011 samples). Water samples collected during October 2011 (unpublished) were processed in the same way as water samples from the 2014 coastal mixing line data set, as described below in detail.

Details on the collection and processing of water samples collected for the 2014 coastal mixing line are presented below. Collection began in April of 2014 and lasted through March of 2015. Unfortunately, data from water samples collected between January and March of 2015 are not yet available and so are not presented here. Water samples were collected monthly in areas accessible by road, primarily east of Penobscot Bay. An effort was made to visit the same locations each month in order to gain a better understanding of regional seasonal variability in water composition. Additionally, water was collected by scientists from the Mount Desert Biological Laboratory and by citizen scientist volunteers at locations throughout the Maine coast convenient to where they lived and worked. Freshwater samples were also obtained from the Penobscot River in Old Town, Maine (44.937642°, −68.646260°) on a monthly basis and from the Kennebec River immediately before the Androscoggin joins it (44.013367°, −69.831106°) several times throughout the year. It is important to note that while it is freshwater, the Kennebec is tidal at this location. Water was collected in either 1 oz or 4 oz french square glass bottles with phenolic polycone lined caps. Every effort was made to fill the bottles to the very top in order to minimize head space in the bottle and consequently evaporation. Water samples were stored in a refrigerator when possible, although this was not always an option.

Water samples were transported to Iowa State University's SIL. Here samples were measured for isotopes on a Picarro L2130-i Isotopic Liquid Water Analyzer with

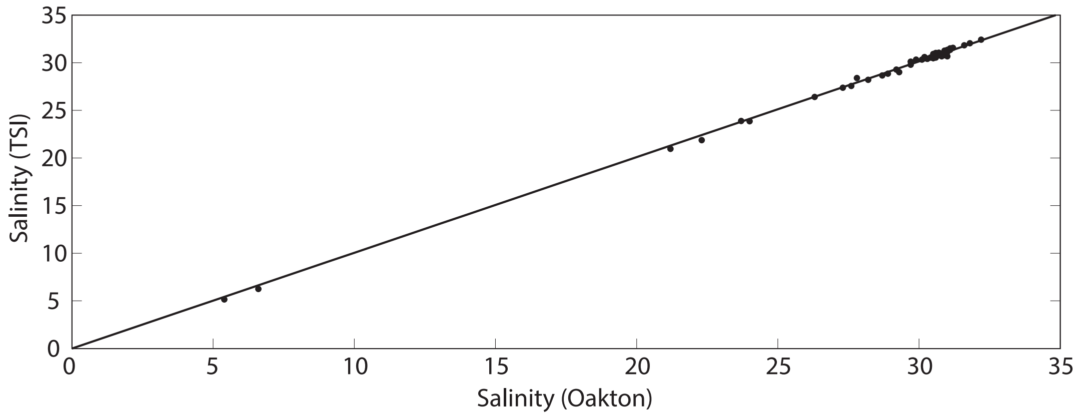

Figure 2.4. Comparison of salinity measurements of the same water sample by two different salinity meters. The two salinity meters are the Oakton SALT 6+ handheld salinity meter (x axis) and the TSI Professional Plus salinity meter (y axis).

an attached autosampler. The isotopic values of samples were calculated using three different reference standards: Vienna Standard Mean Ocean Water (VSMOW), OH-2 and OH-3. In two instances, OH-1 was used instead of OH-2 as a standard. The uncertainty (resulting from analytical uncertainty and average correction factor uncertainty) ranged from ±0.07‰ to ±0.18‰ and averaged 0.12‰.

The salinity of water samples was measured at SIL using a Oakton SALT 6+ handheld salinity meter. To test the accuracy of this meter, salinity of several of the water samples was also measured using a TSI Professional Plus salinity meter. Both salinity meters were calibrated using a $45,000$ μSiemens/cm solution (∼29.16 ppt). The calibration was tested on a 32.0 ppt solution composed of deionized water and pure sodium chloride (NaCl). As is seen in Figure 2.4, the two meters were in close agreement with a slope of 1.004 and a coefficient of determination (R^2 value) of 0.999. Therefore, the salinity values measured using the Oakton SALT 6+ handheld salinity meter are considered to be very accurate.

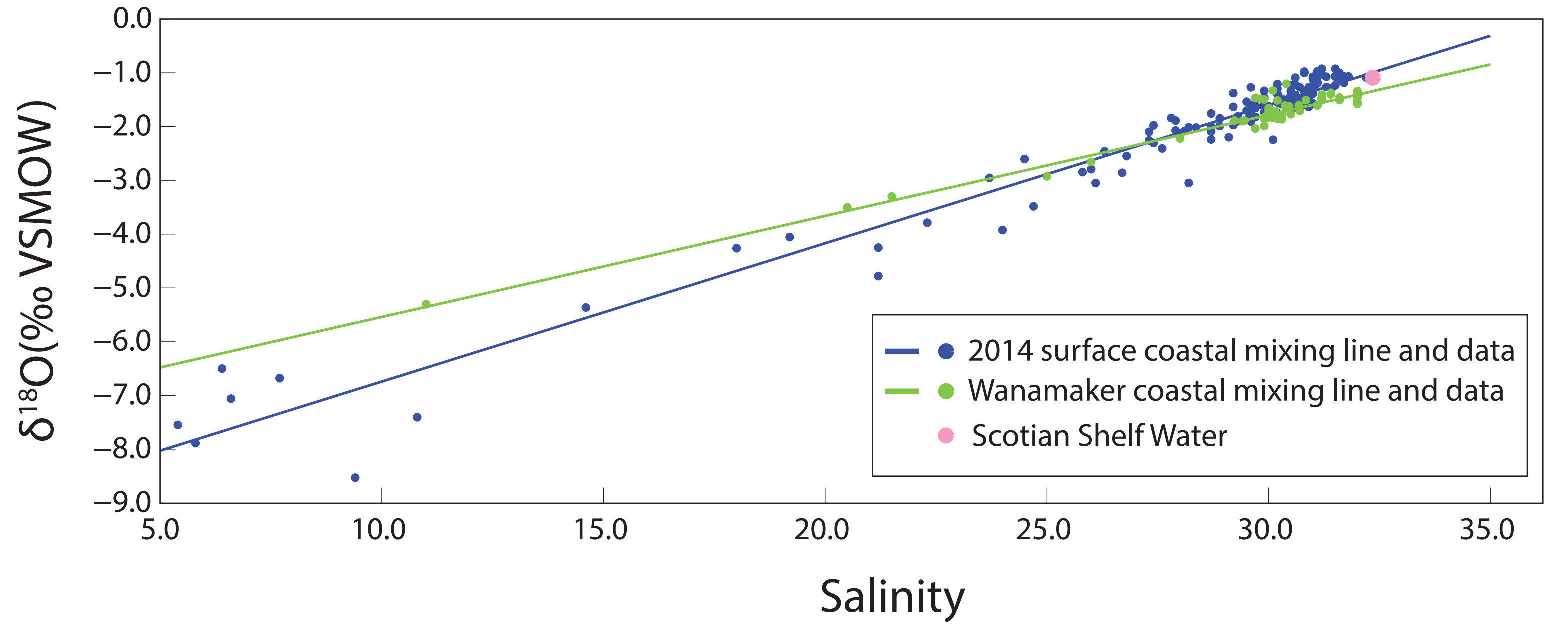

Figure 2.5. Coastal Gulf of Maine δ^{18}O-salinity mixing lines. Also included is the composition of Scotian Shelf Water (SSW) as determined by Chapman et al. (1986). As pointed out by Smith et al. (2001), the oxygen isotope and salinity value of Scotian Shelf water varies from year to year depending on river runoff. This was the value found in the spring of 1981.

2.4 Results

2.4.1 Coastal Gulf of Maine δ^{18}O-salinity mixing lines

The δ^{18}O-salinity relationships for coastal Gulf of Maine waters, derived from both the Wanamaker coastal mixing line data set and the 2014 surface coastal mixing line data set, are presented in Figure 2.5. The equation for the Wanamaker coastal mixing line is:

$$\delta^{18}O_w = 0.2S - 7.4 \tag{2.7}$$

Salinity explains 98.0% of the variance seen in the $\delta^{18}O_w$ values for water samples collected for this mixing line. The equation for the 2014 coastal mixing line is:

$$\delta^{18}O_w = 0.3S - 9.3 \tag{2.8}$$

Salinity explains 95.4% of the variance in the $\delta^{18}O_w$ values for water samples collected for this mixing line. Water samples with salinities below 5 were not used in these mixing lines so as not to significantly influence the mixing line with a freshwater source specific to a given region in the Gulf of Maine.

Figure 2.6 shows the distribution of this data. The median salinity value for the 2014 coastal mixing line data set is 30.2. 50% of the data fall between 30.0 and 31.5. The mean salinity range for the Wanamaker coastal mixing line data set is similar at 30.4. 50% of these data fall between 30.0 and 31.4. The mean $\delta^{18}O_w$ value for water samples in the 2014 coastal mixing line data set is −1.56‰, with 50% of these data falling between −2.00‰ and −1.34‰. The mean $\delta^{18}O_w$ value for the water samples in the Wanamaker coastal mixing line data set is −1.61‰, with 50% of these data falling between values of −1.83‰ and −146‰. As can be seen in Figure 2.6, the 2014 surface coastal mixing line data set contains many more freshwater outliers than the Wanamaker coastal mixing line data set.

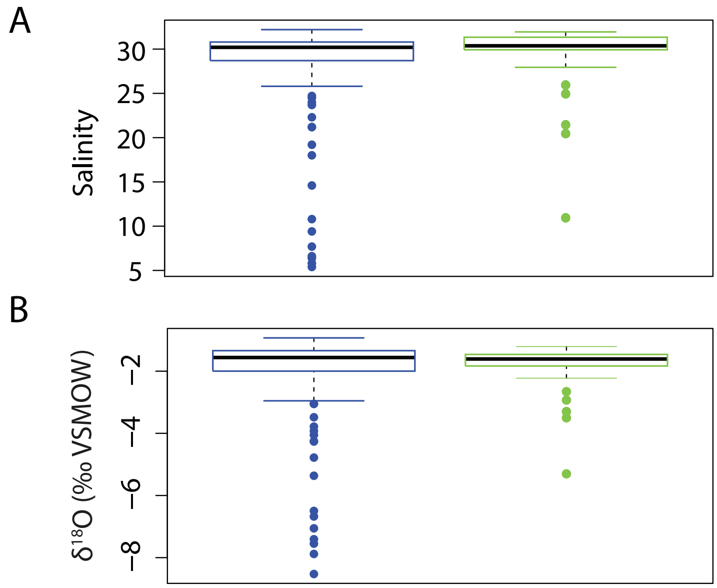

Figure 2.6. Box plots of isotope and salinity data composing the Gulf of Maine coastal mixing lines. These box plots show the distribution of salinity (A) and δ^{18}O (B) values for water samples composing the 2014 surface coastal mixing line (blue, left) and the Wanamaker coastal mixing line (green, right).

Because both data sets contain water samples from the coastal Gulf of Maine, combining them into one mixing line will give a better overall understanding of the relationship between $\delta^{18}\mathrm{O}_w$ and salinity of coastal Gulf of Maine waters. These data together represent the composition of waters in the coastal Gulf of Maine sampled over more than a decade and therefore combining the data into one mixing line reduces the bias towards conditions in any one particular year. The resulting mixing line has the equation:

$$\delta^{18}O_w = 0.2S - 9.0 \tag{2.9}$$

This will be termed the coastal Gulf of Maine mixing line for the remainder of this thesis.

2.4.2 Spatial and seasonal variability in coastal Gulf of Maine water properties

As mentioned in Section 2.3, water samples comprising the 2014 coastal mixing line were collected monthly from April to December at various locations along the eastern coast of Maine to determine spatial and temporal variability of salinity and $\delta^{18}O_w$ values for coastal Gulf of Maine waters. Figure 2.7 shows month to month changes in select locations along the coast (see Figure 2.8 and Table 2.2 for specific locations). This data show a large range in oxygen isotope and salinity measurements. In general, oxygen isotope and salinity values at a given site follow similar trends, as would be expected. Most sites show higher salinity and $\delta^{18}O_w$ values during the summer and early fall months. Salinity and $\delta^{18}O_w$ values in April and May were lower than most of the period sampled. Values tended to also be lower in December than in the summer and fall months.

Figure 2.9 shows water samples from the 2014 coastal mixing line data set plotted in terms of location and colored in terms of $\delta^{18}O_w$ composition. The maps reveal little discernible patterns for the spring and winter with a range of $\delta^{18}O_w$ values present. However, similarities emerge in the summer and fall maps. The majority of samples collected during the summer have values between -1.5‰ and -2.0‰. There are no discernible spatial patterns and all samples have similar $\delta^{18}O_w$ values. The majority of samples collected during the fall are more isotopically enriched than those collected during the summer, with values ranging between -1.0‰ and -1.5‰. Again, there are no discernible spatial patterns and all samples have similar $\delta^{18}O_w$ values. The several samples that have significantly more depleted values than other samples for summer and fall were collected directly from rivers.

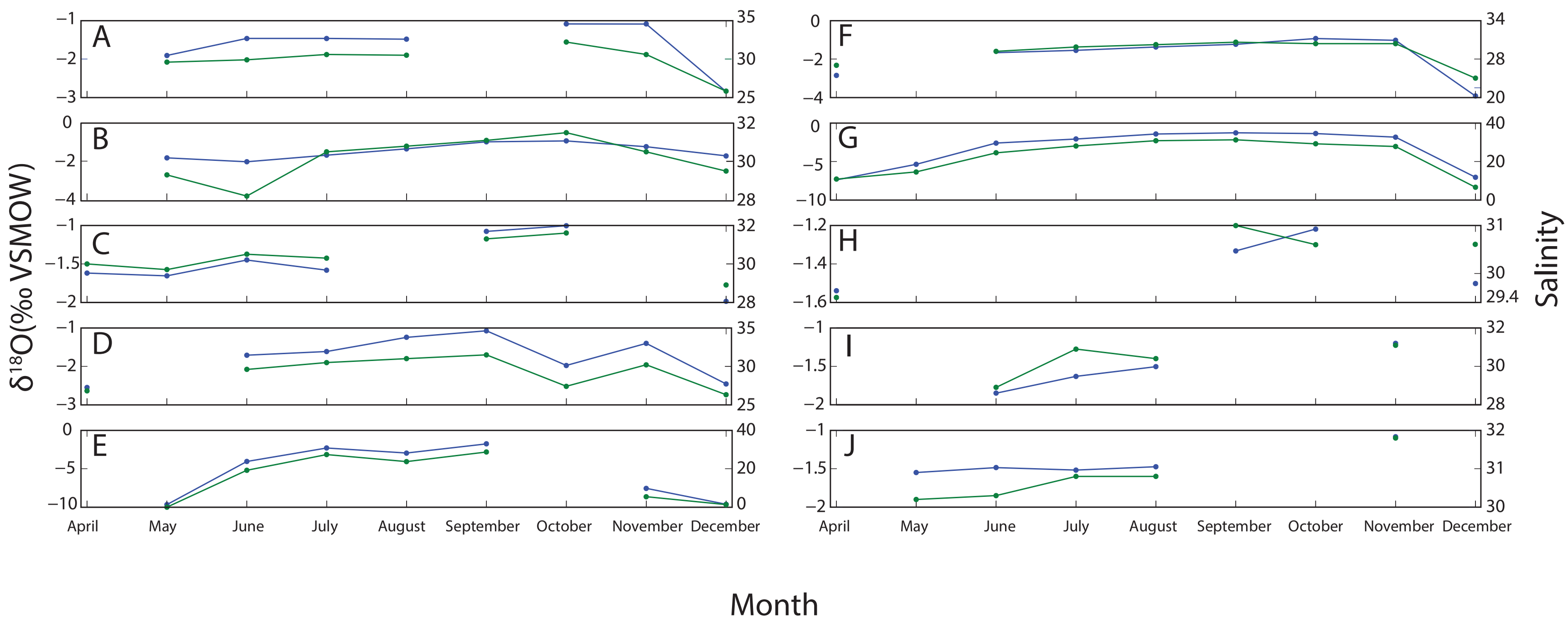

Figure 2.7. Temporal changes in $\delta^{18}O_w$ and salinity values for coastal Gulf of Maine waters in 2014. $\delta^{18}O_w$ values are shown in blue on the left y-axis and salinity values are shown in green on the right y-axis. Panels are organized from most northeast location to most southwest location on the coast of Maine. Refer to Figure 2.8 and Table 2.2 for the specific location where data in each panel was collected.

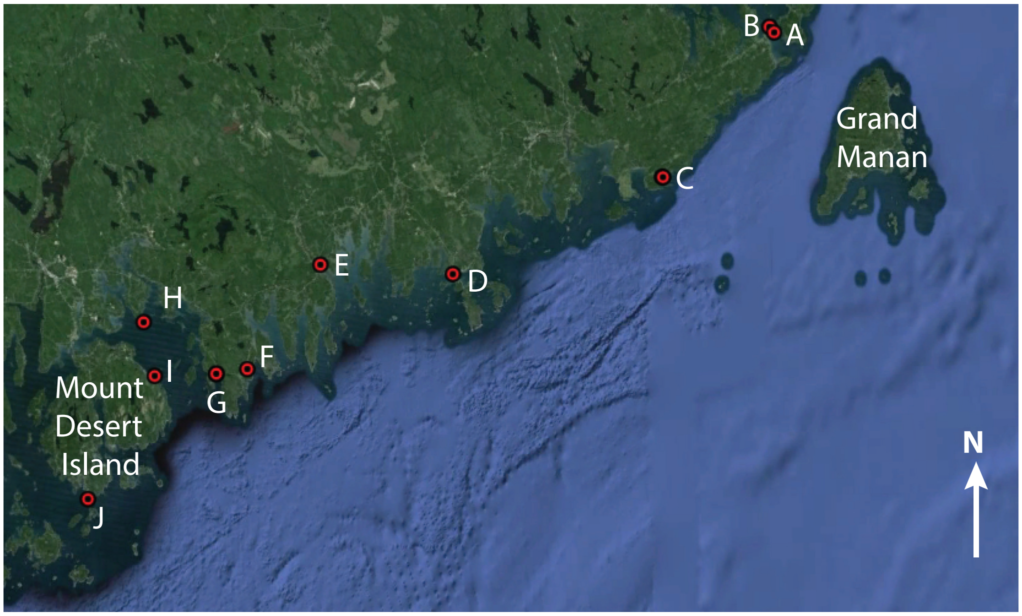

Figure 2.8. Map of monthly water sampling locations. The letters labeling the red markers correspond to the lettered panels in Figure 2.7. The red markers here mark the same location as the red markers in Figure 2.3. For location name and coordinates, see Table 2.2. Map modified from Google Earth.

Panel	Location	Latitude	Longitude
A	Mowry Beach	44.854854°	-66.981424°
B	Lubec	44.862308°	-66.983883°
C	Cutler	44.657318°	-67.207298°
D	Jonesport	44.528216°	-67.620356°
E	Millbridge	44.544268°	-67.878256°
F	Prospect Harbor	44.399638°	-68.023342°
G	Winter Harbor	44.394123°	-68.083946°
H	Sorrento	44.471767°	-68.181868°
I	Bar Harbor	44.392267°	-68.204079°
J	Bass Harbor	44.221642°	-68.336743°

Table 2.2. Table of monthly water sampling location names and coordinates. The panel letters correspond to the panel letters in Figure 2.7 and the letters labeling the red markers in Figure 2.8.

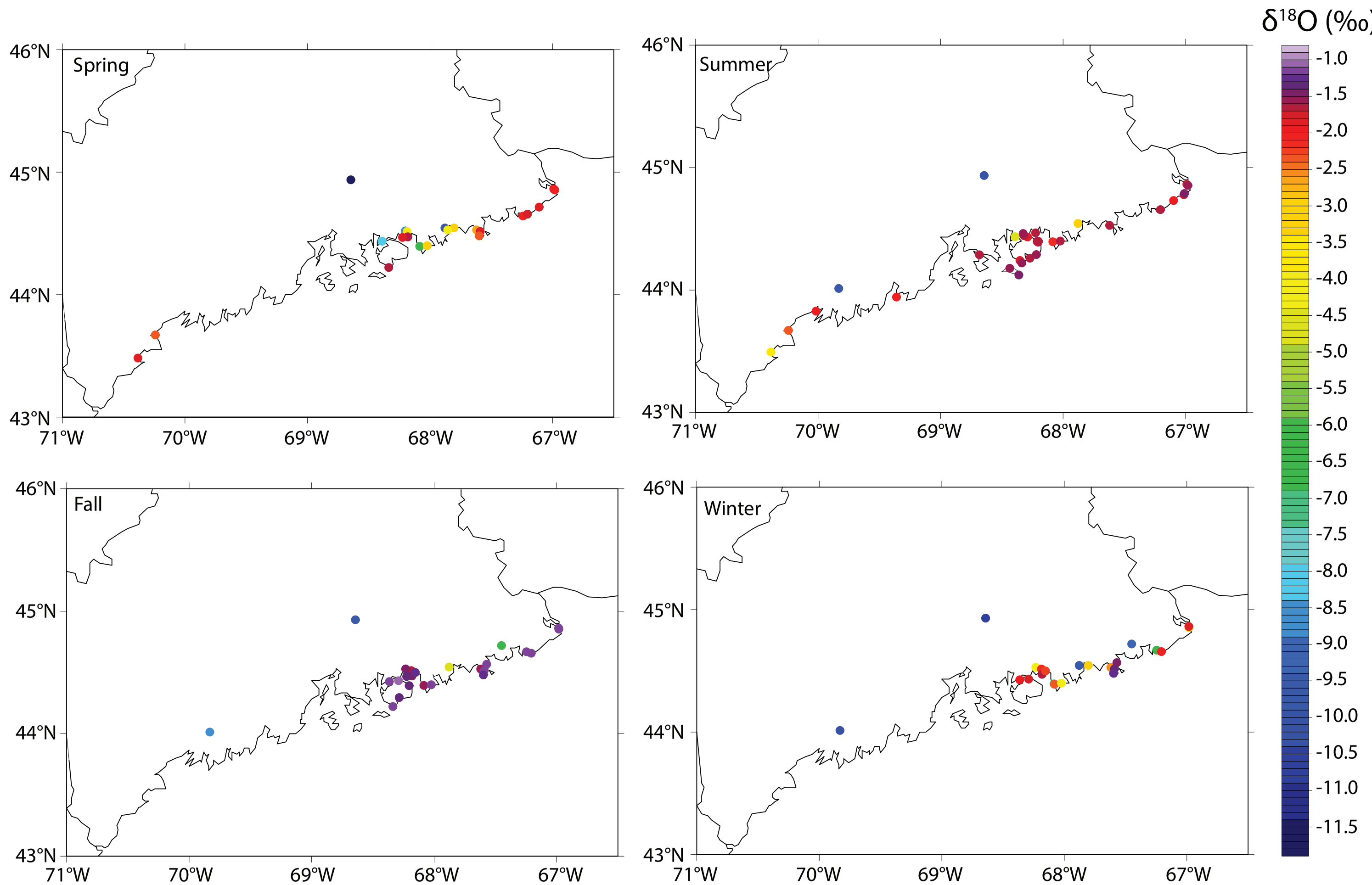

Figure 2.9. Seasonal maps of the $\delta^{18}O_w$ composition of coastal Gulf of Maine waters from water samples collected for the 2014 surface coastal mixing line. Data is organized based on what time of year the sample was collected: Spring (April and May), Summer (June, July, August), Fall (September, October, November), Winter (December). Data collected in January-March are not yet available. Data from water samples collected at the same location during the same season were averaged together.

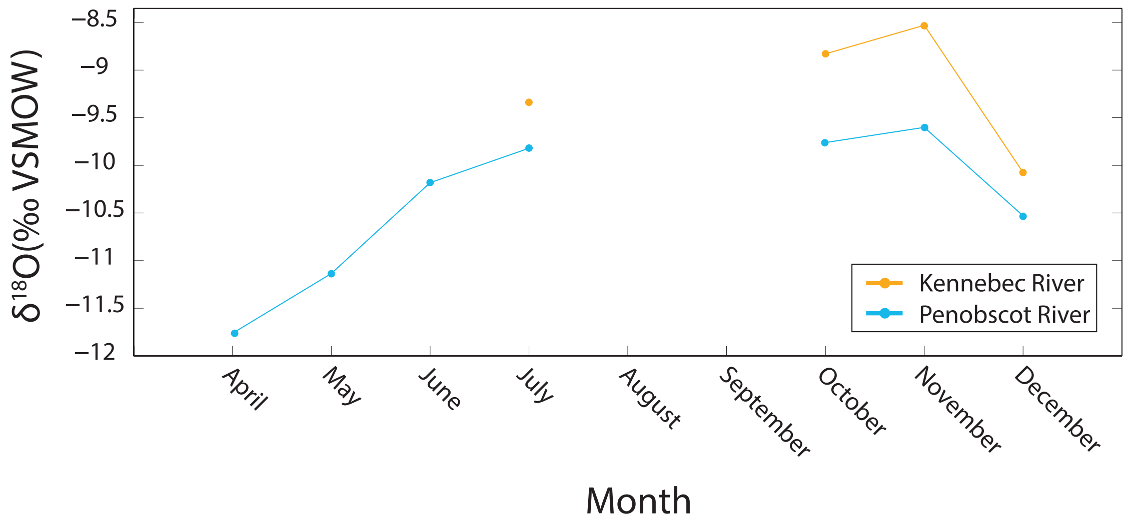

Figure 2.10. Temporal variability of $\delta^{18}O_w$ composition of Maine river water from samples collected in 2014. See text for specific locations.

2.4.3 Temporal changes in the oxygen isotopic composition of Maine rivers

The temporal variability of $\delta^{18}O_w$ values from water samples collected on the Kennebec and Penobscot Rivers is shown in Figure 2.10. The average $\delta^{18}O_w$ value for the Penobscot River is -10.4‰. The average $\delta^{18}O_w$ value for the Kennebec River is -9.2‰. However, it is important to note that these rivers were not sampled in all months and that the Kennebec was sampled in fewer months than the Penobscot. The average $\delta^{18}O_w$ of the Penobscot for the months in which the Kennebec was also sampled (July, October, November and December) was -9.9‰. As shown by these averages and Figure 2.10, the $\delta^{18}O_w$ values of water samples from the Kennebec River are consistently more enriched than those from the Penobscot River. Both rivers show strong differences in $\delta^{18}O_w$ between seasons, with a more than 2‰ difference in the Penobscot River, and follow similar $\delta^{18}O_w$ trends to those seen in the coastal water samples, with more depleted values in April and May, more enriched values during the summer, with peak values in November and becoming more depleted again in December.

2.5 Discussion

2.5.1 Seasonal variability

The seasonal variability seen at most of the locations sampled, of relatively low salinity and $\delta^{18}O_w$ during the spring and early winter months and higher values during the summer and fall months (Figures 2.7 and 2.9), indicates a significant influence of local river water on coastal Gulf of Maine waters, as would be expected. While there is not enough data available to do a strong statistical analysis of the influences on water properties in coastal Gulf of Maine waters, a visual investigation indicates likely influence from both changes in river discharge and changes in river $\delta^{18}O_w$ composition. As was described in Section 2.4.3, the $\delta^{18}O_w$ compositional variability of Penobscot and Kennebec Rivers show similar patterns to $\delta^{18}O_w$ compositional variability of Gulf of Maine coastal seawater (Figure 2.10). The depleted values in April and May are the result of snow melt influences. Because snow forms at colder temperatures, the oxygen isotopes within the snow are more depleted due to higher fractionation factors and increased condensation of water vapor at lower latitudes, leaving the water vapor that reaches the Gulf of Maine more depleted. Therefore, when the snow melts in spring, rivers carry waters that have more depleted $\delta^{18}O_w$ to the Gulf of Maine, clearly influencing Gulf of Maine waters. This seasonal variability in $\delta^{18}O_w$ values of river water can also explain the depleted $\delta^{18}O_w$ values of Gulf of Maine seawater in December. Because of the colder weather, precipitation feeding the rivers during December would also be depleted in $\delta^{18}O_w$.

However, as salinity shows similar seasonal changes to $\delta^{18}O_w$, it is likely that the seasonal changes in river discharge have a significant influence on coastal Gulf of Maine water properties, as would be expected. 2014 average monthly discharges of 5 of the major rivers that empty into the Gulf of Maine is shown in Figure 2.11.

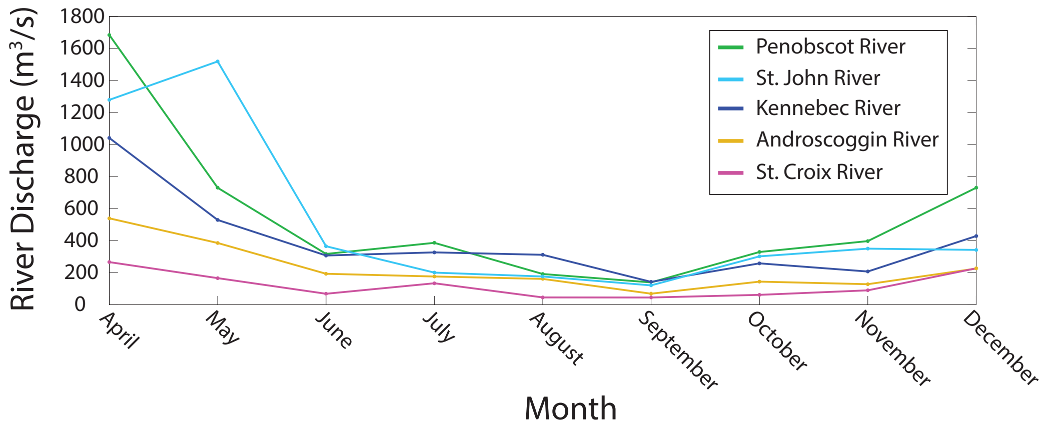

Figure 2.11. 2014 monthly average discharge of select major rivers that empty into the Gulf of Maine. Data taken from the closest available stream gauge to the coast for five rivers: the Penobscot River (45.236111°, -68.651389°), St. John River (47.038889°, -67.739722°), the Kennebec River (44.472222°, -69.683889°), the Androscoggin River (44.072222°, -70.208056°) and the St. Croix (45.136944°, -67.318056°). Data obtained from the Water Survey of Canada (St. John River; http://wateroffice.ec.gc.ca/report/) and the United States Geological Survey (http://waterdata.usgs.gov/usa/nwis/). See Figure 2.3 for the location of each river mouth.

Discharges for all rivers were high in the spring, as a result of snow and ice melt, before significantly diminishing in the summer and fall months. Discharges again increased in December. It is important to note that some of the rivers were frozen for parts of December so the average presented in Figure 2.11 is only an average of those days when the water was flowing. Changes in river discharge would be expected to effect both salinity and $\delta^{18}O_w$ of coastal waters as rivers bring fresh, depleted waters to the coast.

While there is not enough data available to be able to analyze whether variability in river discharge or river $\delta^{18}O_w$ plays a larger role in the variability of coastal Gulf of Maine waters, it is clear that rivers emptying into the Gulf of Maine have a strong influence on these waters. Because salinity changes so closely follow $\delta^{18}O_w$ changes in coastal waters, it seems likely that river discharge variability is the dominant influence on coastal water properties. It is important to note that water property variability in coastal Gulf of Maine waters does not follow precipitation trends for 2014 as recorded in Bangor, Maine, the closest weather station to the area where most of the water samples for this research were collected (not shown). Therefore, it is likely that river discharge and isotopic composition, and not direct precipitation, have the most influence on water properties of coastal Gulf of Maine waters.

2.5.2 Spatial variability

The influence of rivers on coastal Gulf of Maine waters is also evident when looking at the spatial variability of δ^{18}O values (Figure 2.9). During the spring and winter seasons, where river runoff is greatest as noted above, there seem to be few spatial similarities or patterns in the $\delta^{18}O_w$ composition of coastal Gulf of Maine waters. The $\delta^{18}O_w$ composition of water samples collected during these high freshwater discharge periods is likely dependent on proximity of the sample to a freshwater source and the $\delta^{18}O_w$ of that freshwater source.

As stated above, rivers in the eastern Gulf of Maine tend to be more isotopically depleted than those in the western Gulf of Maine and therefore one might expect to see $\delta^{18}O_w$ values becoming more enriched to the west. However, small rivers that do not have large watersheds extending into higher latitudes, which is the case for many of the rivers that empty into the Gulf of Maine near where water samples were collected, will not be as depleted as those rivers with larger watersheds. Therefore, the data collected in the spring and winter months likely reflects the influence of local river $\delta^{18}O_w$ composition and shows little spatial patterns due to the large variety of watershed size for these local rivers.

Figure 2.9 clearly shows that water samples collected during the fall were more isotopically enriched than those collected during the summer and that water samples from both seasons were more isotopically enriched than sample collected during spring and winter. In the previous section, I suggested that these seasonal differences were evidence of less influence of freshwater on coastal water properties during these the summer and fall months due to decreased river discharge. The fact that water samples collected during the summer and fall seasons show within-season similarities also suggests decreased local river water influence. With decreased local river influence, coastal seawater composition is primarily determined by the composition of waters carried by ocean currents, specifically the Eastern Maine Coastal Current (EMCC) in this case. As that composition is fairly uniform throughout the area sampled, water samples collected along the eastern Maine coast show similar composition for seasons when river discharge is low.

2.5.3 Gulf of Maine mixing lines

Both of the coastal Gulf of Maine mixing lines that I present in this paper indicate mixing between two distinct end-members: SSW and MRW. As can be seen in Figure 2.5, the Wanamaker coastal mixing line has a slightly more enriched freshwater end member than the 2014 surface coastal mixing line. This difference in the freshwater end member is likely the result of differences in location where the samples were collected. Most of the samples collected for the Wanamaker mixing line were collected in the western Gulf of Maine while most of the samples for the 2014 mixing line were collected in the eastern Gulf of Maine (Figure 2.3). The differences in latitude between these general locations leads to differences in the $\delta^{18}O_w$ signature of the water feeding these regions as rivers flowing into the eastern Gulf of Maine tend to have watersheds at higher latitudes and therefore are more isotopically depleted. These differences can be clearly seen from the rivers sampled for this study (Figure 2.10). The Kennebec River, one of the major rivers that empties into the western Gulf of Maine, was consistently more isotopically enriched than the Penobscot, one of the major rivers that empties into the eastern Gulf of Maine. While these spatial differences in $\delta^{18}O_w$ are not seen when looking at locations sampled for the 2014 coastal Gulf of Maine mixing line (Figure 2.9), this lack of latitudinal differences is likely due to the relatively small area where samples were collected (i.e. almost exclusively from the eastern Gulf of Maine), and the obvious influence from small local rivers which tend to have small, lower latitude watersheds, as discussed in Section 2.5.2. Therefore, it is logical that the Wanamaker mixing line would have a more enriched freshwater end member than the 2014 mixing line.

Interestingly, the freshwater end member for the 2014 mixing line had a $\delta^{18}O_w$ value of $-9.3‰$, which is enriched by approximately 1‰ compared to the average value of the Penobscot for the months sampled ($-10.40‰$). This more enriched freshwater end member again suggests the influence of small local rivers, which have smaller watersheds and are therefore more enriched than the Penobscot River (see Section 2.5.2), on coastal water samples.

As pointed out by Smith et al. (2001) and others, the composition of SSW changes from year to year as a result of changes in river runoff onto the Scotian Shelf. Figure 2.5 shows the estimated composition of SSW, as measured in the spring of 1981 by Chapman et al. (1986), to be the saline end member of the 2014 mixing line. The Wanamaker mixing line has a slightly more depleted saline end member, which is likely due to differences in SSW composition in the Gulf of Maine between 2014 and the years the samples collected for the Wanamaker mixing line were taken (2003-2013). A more depleted SSW would likely indicate less river runoff onto the Scotian Shelf so that a greater percent of the freshwater contributing to SSW composition was from higher latitudes with a more depleted oxygen isotopic signature. When these two data sets are combined to form the coastal Gulf of Maine mixing line (equation 2.9), the saline end member is clearly SSW (Figure 2.12).

When comparing the coastal mixing lines to other mixing lines found for waters in the Gulf of Maine and surrounding regions (equations 2.3, 2.4, 2.5, and 2.6), the coastal mixing line has the most enriched freshwater end member. This result is

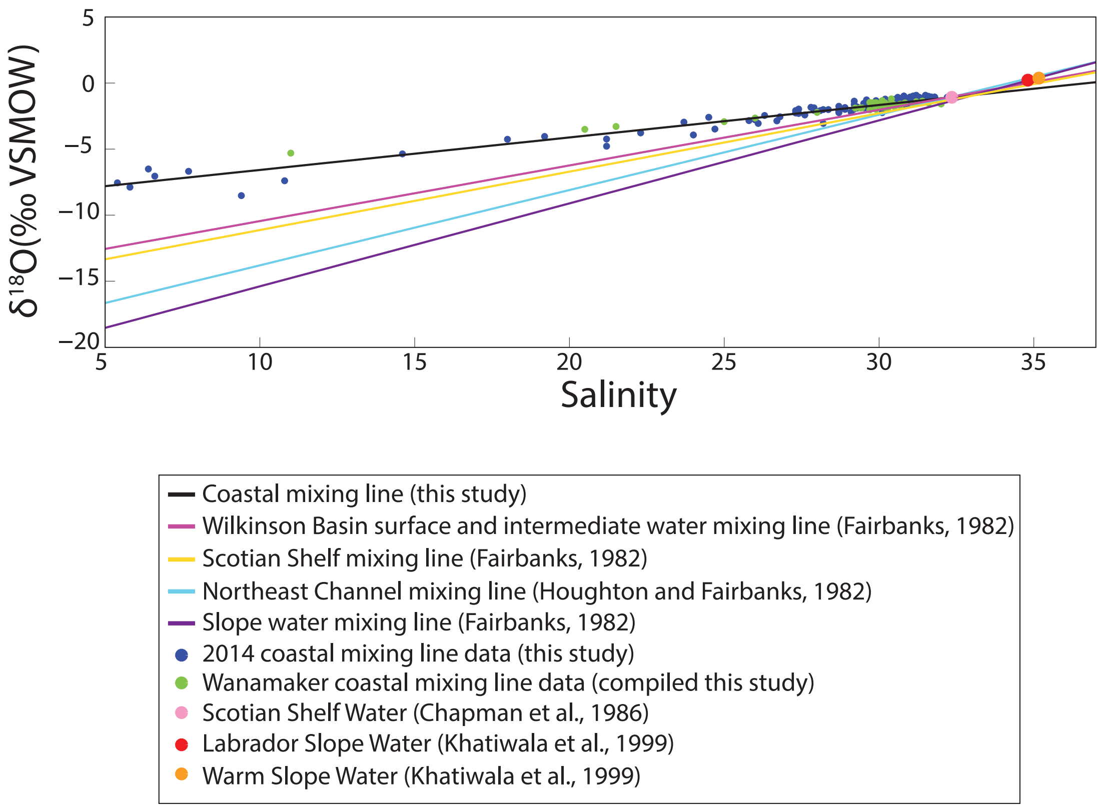

Figure 2.12. $\delta^{18}O_w$-salinity mixing lines for the Gulf of Maine along with data from the Wanamaker coastal mixing line and the 2014 surface coastal mixing line. The coastal mixing line derived by combining data from the Wanamaker coastal mixing line and 2014 surface coastal mixing line data sets (equation 2.9); the Fairbanks (1982) Wilkinson Basin surface and intermediate water mixing line (equation 2.3); the Fairbanks (1982) Scotian Shelf mixing line (equation 2.4); the Houghton and Fairbanks (2001) Northeast Channel mixing line (equation 2.6); the Fairbanks (1982) slope water mixing line (purple; equation 2.5). Water masses are plotted using the bolded values in Table 2.1.

consistent with the general assumption that coastal Gulf of Maine surface waters are influenced by local river runoff while waters found at deeper depths and farther from the coast are influenced by more depleted freshwater sources originating in the Gulf of St. Lawrence and the Labrador Shelf (Houghton and Fairbanks, 2001).

The coastal Gulf of Maine mixing line falls farther away from WSW and LSW end members than any of the other mixing lines found for the region, indicating little if any influence from deep slope waters. This result implies that slope waters are not being mixed all the way to the surface along the coast in the Gulf of Maine. The water samples that were collected for the coastal Gulf of Maine mixing line that have more depleted $\delta^{18}O_w$ values than most of the samples in this data set may be composed of some slope water as they fall closer to mixing lines that have WSW and LSW as end members.

It is important to note that previously constructed mixing lines from the Gulf of Maine and surrounding regions were composed of water samples with salinities of no less than 30, since fresher samples were not present in the regions where water samples were collected for these mixing lines. Therefore, the freshwater end member of these mixing lines is less constrained than it is for the coastal Gulf of Maine mixing line.

2.5.4 Implications for Gulf of Maine paleoclimate

Understanding the relationship between $\delta^{18}O_w$ and salinity in the Gulf of Maine is useful for both understanding hydrographic dynamics in the region today but also in reconstructing this hydrography in the past. Specifically, as mentioned in Chapter 1 of this thesis and described in depth in Chapter 3, using oxygen isotopes archived in *Arctica islandica* shells or other carbonate material to reconstruct water temperatures requires knowledge of the $\delta^{18}O_w$ composition in which that material formed. While this is generally not available, understanding the relationship between

$\delta^{18}O_w$ and salinity in a region and using instrumental records of the salinity in the area to reconstruct $\delta^{18}O_w$ at least provides an estimate of the general conditions in the area of reconstruction. Constructing these $\delta^{18}O_w$-salinity mixing lines also allows for a general understanding of hydrographic dynamics in the region today, which is useful when interpreting reconstructed hydrographic variability in the past.

As can be seen from the data presented here, there is a significant difference in mixing lines between coastal waters and more offshore waters. Therefore, depending on where the proxy material is collected from, the mixing line used for reconstructing water temperatures must be carefully considered. For example, the material used for hydrographic reconstructions in this thesis (Chapter 3), was collected at ~38 meters depth just off the coast in the western Gulf of Maine. Therefore, it is likely that using a coastal mixing line such as the one presented here will allow for a more accurate estimate of $\delta^{18}O_w$ from instrumental records of salinity in the area than those mixing lines constructed from water samples collected in offshore locations, such as Wilkinson Basin (equation 2.3; Fairbanks, 1982) and the Northeast Channel (equation 2.6; Houghton and Fairbanks, 2001). However, it is important to emphasize that this coastal mixing line is only derived from water samples collected near or at the surface. More data collection is needed in order to better constrain the $\delta^{18}O_w$-salinity relationship at depth where the proxy material used in this thesis was collected.

2.5.5 Conclusions and future work

$\delta^{18}O_w$ and salinity values measured in water samples collected along the coastal Gulf of Maine from 2003-2014 are presented. These data reveal that coastal Gulf of Maine waters fall along a mixing line between MRW and SSW. The freshwater end member of this mixing line varies depending on the location that the water sample was collected, with a more enriched end member for samples collected in the western

Gulf of Maine. These coastal surface waters do not appear to be comprised of any slope water.

The $\delta^{18}O_w$ and salinity composition of these waters are influenced primarily by changes in river discharge and $\delta^{18}O_w$ variability of Maine rivers, as evident from the seasonal trends in salinity and coastal $\delta^{18}O_w$, with lower salinity and $\delta^{18}O_w$ values in early winter and spring, following trends in river discharge and $\delta^{18}O_w$ composition. The effect of changes in river discharge on coastal Maine water properties is also evident from looking at spatial differences is $\delta^{18}O_w$ values: large spatial differences in spring and winter indicate the increased influence by local rivers while few spatial difference in summer and fall indicate larger ocean water influences.

This paper offers a start to understanding $\delta^{18}O_w$-salinity relationships as well as hydrographic variability and major driving influences of water properties in coastal Gulf of Maine waters. However, there is a lot of work left to be done in order to develop a clearer picture of water properties in the region. Most notably, water samples from January, February and March are needed for a full understanding of seasonal variability in the coastal waters. Those water samples have already been collected and are awaiting processing so a full annual record of $\delta^{18}O_w$ and salinity in coastal waters will soon be available.

Additionally, no work has been done to look at changes in the $\delta^{18}O_w$-salinity relationship with depth in the Gulf of Maine except for a few select locations (Wilkinson Basin - Fairbanks, 1982; the Northeast Channel - Houghton and Fairbanks, 2001). Understanding how these water properties change with depth throughout the Gulf of Maine will facilitate a much better picture of hydrographic dynamics with depth as well as providing a mixing line for reconstructing paleoclimate material collected at depth.

Chapter 3

RECONSTRUCTING LATE HOLOCENE HYDROGRAPHIC VARIABILITY IN THE GULF OF MAINE USING OXYGEN ISOTOPES FROM AN *ARCTICA ISLANDICA* SHELL-BASED RECORD

3.1 Chapter abstract

This paper seeks to address the need for a long-term record of hydrographic variability in the Gulf of Maine by compiling an annually resolved record of oxygen isotopes measured in precisely dated *Arctica islandica* shells collected at ∼38 meters water depth off of Seguin Island in the western Gulf of Maine. This record spans the time period between 1695 and 1915. Seawater temperatures calculated from this record vary by as much as ∼11°C, from 2.4°-13.5°C. These calculations suggest a broader range of Gulf of Maine average annual seawater temperatures than previously thought. Combined with the oxygen isotope record published by Wanamaker et al. (2008*a*), this oxygen isotope record suggests centennial-scale oscillations in seawater temperatures over the last 1000 years, indicating fluctuations in the dominant water mass influencing Gulf of Maine hydrographic properties. This temperature record does not indicate cooling in the Gulf of Maine as had been previously suggested.

The correlation between this record and sea surface temperatures (SSTs) in the North Atlantic during the fall and early winter suggests a negative correlation with SSTs in the western North Atlantic ($r>-0.5$) but a positive correlation ($r>0.6$) with those in the Labrador Sea/subpolar gyre region. Such a dipole pattern of correlation is indicative of Atlantic meridional overturning circulation (AMOC) influence, as suggested by several modeling studies. This record showed a small but significant

correlation with the Atlantic Multidecadal Oscillation (AMO) but no correlation with the North Atlantic Oscillation (NAO) index, which had previously been thought to be the main driver of Gulf of Maine hydrographic variability based on the limited instrumental record.

The seawater temperature reconstruction presented in this paper suggests that recent warming in the Gulf of Maine is not outside the natural range of temperatures in the region over the last 300 years. Therefore, such warming can not be unequivocally attributed to anthropogenic climate change. However, the negative correlation between AMOC strength and Gulf of Maine temperatures that this record suggests indicates future warming of the Gulf of Maine with the predicted weakening of AMOC strength.

3.2 Introduction

The consequences of increased atmospheric greenhouse gases since the beginning of the industrial revolution have been felt around the world in the form of increased frequency in extreme weather events, rising sea levels and increased air and water temperatures (IPCC, 2013). One place where recent apparent climatic changes have warranted a lot of discussion is the Gulf of Maine, a semi-enclosed basin on the east coast of North America (Figures 3.1 and 3.2). Recent studies and observations have suggested that major hydrographic changes are currently ongoing in the Gulf of Maine, both in terms of sea surface temperatures (SSTs) as well as water mass dominance, possibly as a result of the broader climatic changes seen globally (Mills et al., 2013; Pershing et al., 2014; Smith et al., 2012; Townsend et al., 2010). Although the Gulf of Maine region enjoys a relatively rich history of scientific research, starting with the investigations of Henry Bigelow in the early 1900s (Bigelow, 1927), the period of observations and instrumental records is not long enough to get an

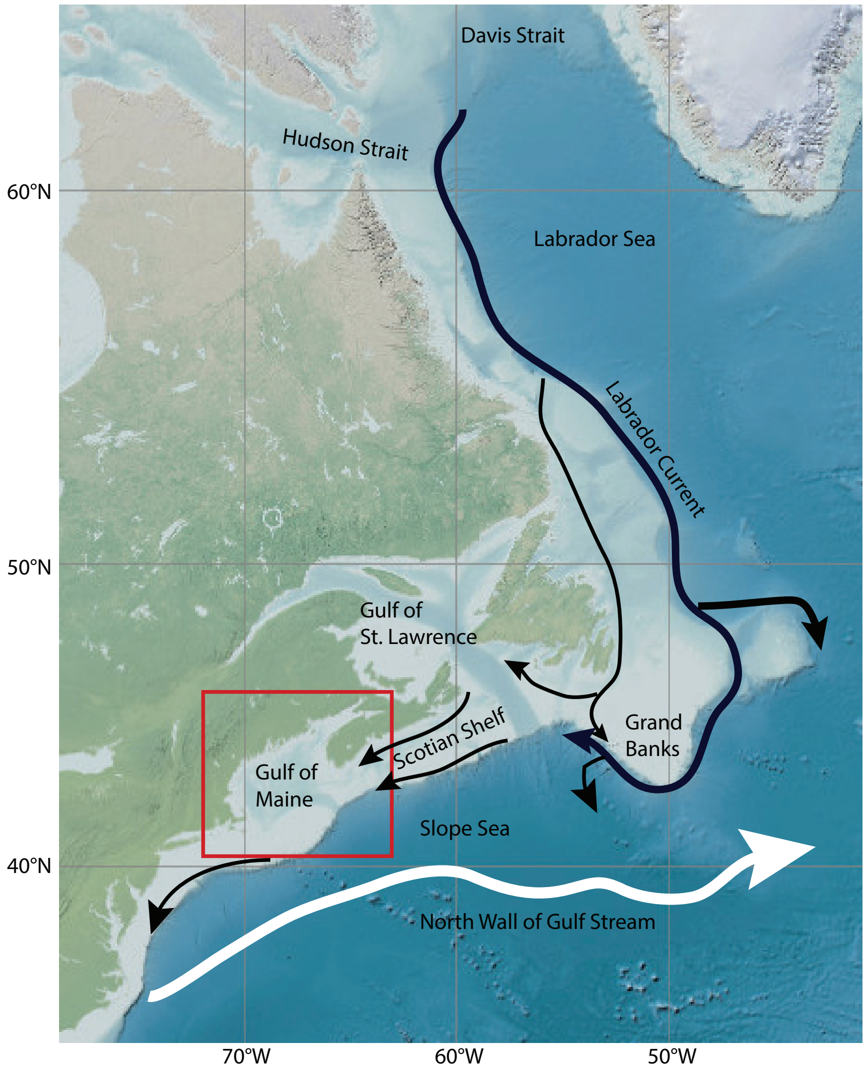

Figure 3.1. Map of the major currents in the western North Atlantic. Currents shown include the Gulf Stream (white arrow) and the Labrador Current (black arrows). Current locations and orientations after Chapman and Beardsley (1989) and Loder et al. (1998). Map modified from Townsend et al. (2010). Width of arrows indicates the approximate relative strength of currents. The red box marks the location of the Gulf of Maine and marks the location of Figure 3.2. Map modified from the NOAA National Geophysical Data Center (maps.ngdc.noaa.gov/viewers/fishmaps).

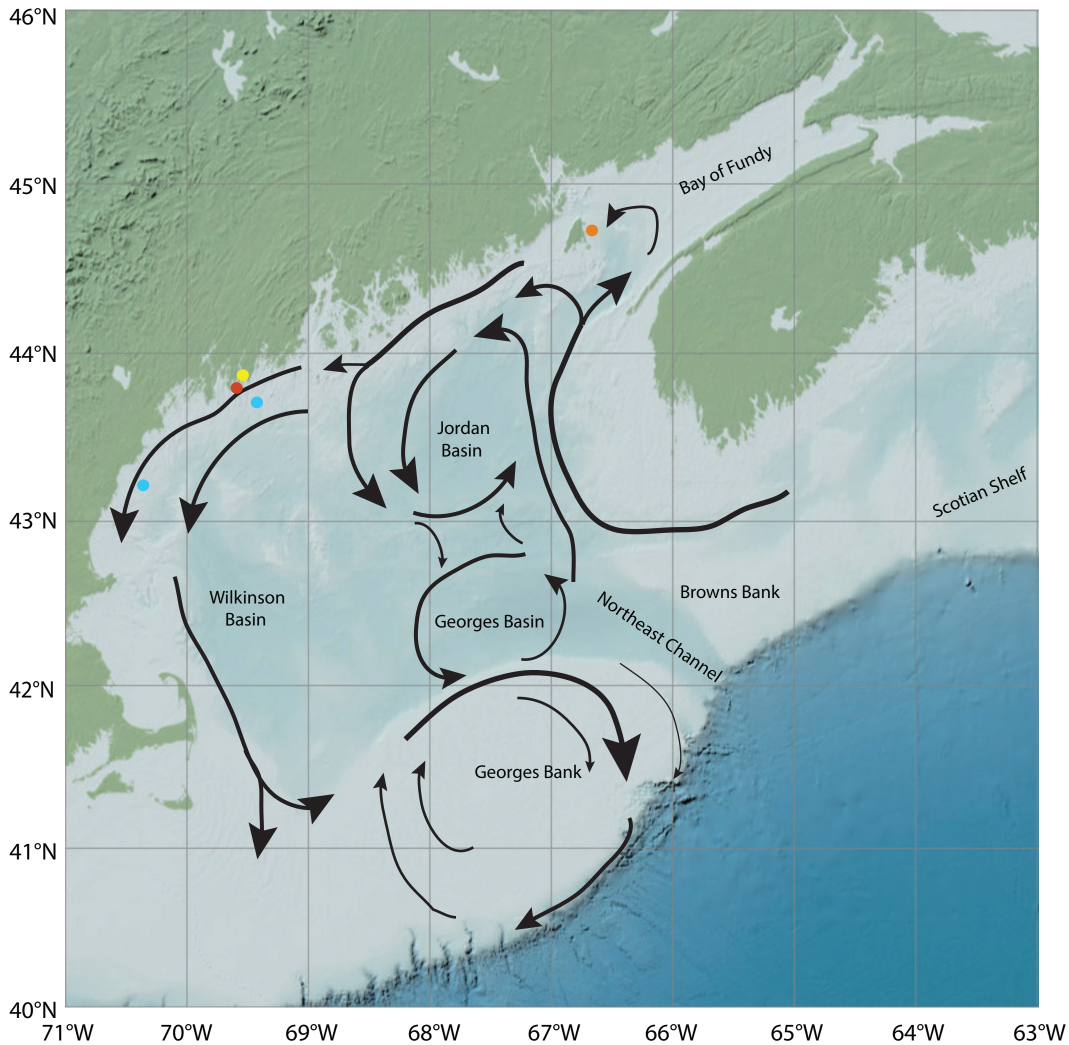

Figure 3.2. Map of the Gulf of Maine. Major geographic features are labeled. Major surface currents are shown by the arrows with the width of the arrow indicating the approximate relative strength of the current. Based on Pettigrew et al. (2005). The yellow dot marks the location of the Boothbay Harbor Environmental Monitoring Program station. The orange dot marks the location of the Prince 5 station. The blue dots mark the location of the two NERACOOS buoys discussed in the text (B01 is to the west of E01). The red dot marks the location off of Seguin Island where *Arctica islandica* shells were collected for the research presented in this thesis. Map modified from the NOAA National Geophysical Data Center (maps.ngdc.noaa.gov/viewers/fishmaps).

accurate picture of the natural variability and climate drivers of the Gulf of Maine. Without this knowledge, it is difficult to determine whether the recent changes observed in the Gulf of Maine are the result of natural variability in the system or the consequence of anthropogenic climate change. The research presented in this paper seeks to reconstruct 220 years of hydrographic changes in the Gulf of Maine, particularly those related to seawater temperature variability, using oxygen isotopes from *Arctica islandica* shells, an annually resolved, absolutely-dated climate proxy. The goal of this research is to gain a better understanding of the natural variability in the Gulf of Maine system and the regional and hemispheric drivers of this variability in order to asses the recent changes seen in the Gulf of Maine in a temporal context.

3.3 Background

3.3.1 Influences on seawater temperatures in the Gulf of Maine

The significant interannual variability in seawater temperatures present in the Gulf of Maine and surrounding region (Weare, 1977) has elicited many studies that sought to understand the source for these temperature fluctuations. Bigelow (1927) was one of the first to comment on this variability when he suggested that changes to the volume of water entering the Gulf of Maine through the Northeast Channel dictated the changes in temperature and salinity seen at depth in the Gulf of Maine. Later studies revised this understanding to suggest that temperature and salinity fluctuations were in fact due to changes in the origin of the slope water entering the Northeast Channel and not the actual volume of that water, with cold bottom waters suggesting a higher proportion of water originating from the Labrador Sea (Colton Jr., 1968; Worthington, 1964). Gatien (1976) defined the specific slope waters entering the Gulf of Maine as Warm Slope Water (WSW) and Labrador

Slope Water (LSW). The author describes WSW as a well-mixed water mass found adjacent to the Gulf Stream at 0-400 meters depth. He defines LSW as a poorly-mixed water mass found below WSW and close to the continental shelf. Further research has found that WSW is a mixture of Gulf Stream Water, North Atlantic Central Water and local shelf waters while LSW can be found on the slope of the Scotian Shelf and is comprised of waters carried by the Labrador Current (Chapman and Beardsley, 1989). The two slope waters are most different in temperature, with LSW being significantly colder than WSW (Gatien, 1976). Additionally, LSW has been shown to have a lower salinity and nutrient content compared to WSW (Gatien, 1976; Townsend and Ellis, 2010; Townsend et al., 2006).

Scotian Shelf Water (SSW) is the third major water mass that influences temperatures in the Gulf of Maine. SSW is relatively cool and fresh (e.g. Pettigrew et al., 1998) and flows into the Gulf of Maine at the surface around Cape Sable, Nova Scotia via the Nova Scotian current (Smith, 1983). SSW has been shown to be a mixture of Newfoundland and Labrador shelf waters as well as waters originating from the Gulf of St. Lawrence (Houghton and Fairbanks, 2001).

There have been numerous studies done on what causes the fluctuation in proportion of WSW and LSW that drives the hydrographic variability in the Gulf of Maine. Petrie and Drinkwater (1993) tested two hypotheses put forward by Lauzier (1965), who suggested that long term temperature variability in the Gulf of Maine and the Scotian Shelf were the result of changes to the proportion of slope waters entering the two regions but could also be the result of changes in the composition of slope water itself. The authors looked at temperature and salinity data from 1945-1990 in the Gulf of Maine and the Bay of Fundy and found a correlation between temperature changes and Labrador Current transport. With increased Labrador Current transport, Labrador Waters extend as far south as the Mid-Atlantic Bight (MAB) and consequently, Gulf of Maine waters become cooler, as happened during the cooling and freshening period between 1952 and 1967. With reduced transport, Labrador Waters only make it as far south as the Laurentian Channel in the Gulf of St. Lawrence. While Petrie and Drinkwater (1993) did find that LSW composition changed over time, these changes were not correlated with changes in temperature and salinity seen in the Gulf of Maine or on the Scotian Shelf. The authors also note that the orthogonal function analysis performed by Thompson et al. (1988) to assess the effect of wind strength on SSTs suggested wind explained a maximum of 24% of the SST variability. However, they point out that further modeling studies by Umoh (1992) suggest that surface heat fluxes only explain 1% of SST variability so it is likely that winds do not play a huge part in seawater temperature variability.

Petrie and Drinkwater (1993) do not suggest a reason for the variability in the strength of the Labrador Current over time. Myers et al. (1989) proposed that the Labrador Current strength is correlated with the North Atlantic Oscillation (NAO). The NAO is defined as the difference in sea surface pressure between the Icelandic low pressure zone and the Azores high pressure zone. A positive (negative) NAO mode corresponds to a larger (smaller) than average gradient between the two zones and stronger (weaker) westerly winds in the Labrador Sea region.

Myers et al. (1989) found a negative correlation between baroclinic transport of the Labrador Current and the NAO. The authors explained this correlation by suggesting that the stronger (weaker) westerly winds associated with a winter NAO positive (negative) mode cause more (less) mixing of offshore waters, bringing more (less) cool and fresh water to the surface and therefore decreasing (increasing) the across shelf density gradient from the shore (which is fresher due to river runoff) to the outer portion of the Labrador Current, decreasing (increasing) the baroclinic transport. Similarly, while investigating the reasons for the extremely cold waters in the MAB region during the early 1880s, Marsh (2000) used a general circulation model to show that the across shore density gradient near the Labrador Sea increased after NAO negative modes, although the model did not explicitly suggest a reason for this increase. The model did show a strengthening of the North Atlantic subpolar gyre with decreased winds associated with a NAO negative mode. The authors suggest their findings indicate that the baroclinic transport of the North Atlantic subpolar gyre decreases over time with prolonged NAO negative modes but the barotropic transport of the North Atlantic subpolar gyre briefly increases with the associated weaker winds, strengthening the outer branch of the Labrador Current and consequently bringing colder waters to regions near the Gulf of Maine.

Drinkwater et al. (1998) also suggested that colder waters found on the Scotian Shelf and in the Gulf of Maine, this time in 1997 and the spring of 1998, were the result of a NAO negative mode two winters before. LSW was found on the Scotian Shelf and in the Gulf of Maine during late 1997 and early 1998, as indicated by a temperature drop of $2-4°C$ as well as a salinity drop in these areas. The authors noted that the likely cause for this infiltration of LSW after the warm period of the 1990s was the significant drop in the NAO index in the winter of 1996, the largest decrease of the 100-year NAO record up to that point.

Petrie (2007) directly addressed the possibility of a correlation between NAO modes and water temperatures in the western North Atlantic, including the Gulf of Maine, by analyzing the correlation between water temperatures and the NAO index from 1970-2004. The author found negative NAO anomalies in preceding years led to decreased water temperatures in the Gulf of Maine and the Scotian Shelf of up to 0.7°C while areas on the Newfoundland-Labrador Shelf, the Gulf of St. Lawrence and the eastern Scotian Shelf had negative correlations with the NAO index in previous years. The author found the strongest correlations between water temperature and the NAO index in bottom waters. When comparing these results to local weather patterns, the author found that the NAO index explained more of the variation in water temperature than the local meteorological data in most cases.

The author suggested that the differences in correlations with the NAO between the different regions of the western North Atlantic is due to a potentially more direct effect of meteorological forcings on the Newfoundland-Labrador Shelf, the Gulf of St. Lawrence and the eastern Scotian Shelf, where negative NAO anomalies indicate weaker winds and less storms, leading to warmer waters in these regions. The western Scotian Shelf and the Gulf of Maine appear to be more significantly influenced by the changes in Labrador Current associated with changes in the NAO index, as suggested by other authors (Marsh, 2000; Myers et al., 1989), so that negative NAO anomalies lead to negative seawater temperature anomalies.

From the above review, it is clear that a significant number of the studies on the causes of Gulf of Maine hydrographic variability have focused on the NAO as it affects the strength of the Labrador Current. The NAO also appears to influence the position of the Gulf Stream and therefore possibly the proportion of different slope waters entering the Gulf of Maine. Taylor and Stephens (1998) noted that the correlation between the position of the north wall of the Gulf Stream and the mode of the NAO two years previous. The authors showed that the Gulf Stream, which is the western boundary current of the wind-driven North Atlantic gyre (Stommel, 1958) and therefore is affected by changes in the wind-patterns, moves to the south (north) two years following a negative (positive) NAO mode, indicating decreased (increased) westerly winds. Therefore, following an NAO negative mode, WSW, which forms adjacent to the Gulf Stream, is farther away from Gulf of Maine, thus decreasing the proportion of WSW entering the Gulf of Maine. At the same time, a southward shift of the Gulf Stream allows more LSW to move around the Tail of the Grand Banks and reach the Gulf of Maine (Rossby, 1999).

While the majority of recent research on Gulf of Maine hydrographic variability has focused on the NAO as a primary forcing, other potential drivers must also be assessed. One plausible driver is the Atlantic Multidecadal Oscillation (AMO), which is an oscillation in sea surface temperature anomalies in the North Atlantic. The AMO has a periodicity of ∼70 years (Delworth and Mann, 2000) and has been shown to have a significant effect on air temperatures in Europe (Folland et al., 1986), hurricane formation in the Atlantic Ocean (Goldenberg et al., 2001), precipitation patterns in both western Europe and North America (Enfield et al., 2001) and glacial extent in the Swiss Alps (Denton and Broecker, 2008). The AMO has been attributed to variability of the Atlantic meridional overturning circulation (AMOC; Delworth and Mann, 2000; Knight et al., 2005; Zhang, 2008). However, there is no empirical evidence to support this association. Additionally, a recent reconstruction of the AMOC did not show an oscillation of 50-70 years and therefore was inconsistent with the periodicity of the AMO (Rahmstorf et al., 2015). Consequently, the association between these two climate drivers is unclear. It is reasonable to suggest that Gulf of Maine SSTs would fluctuate with broader North Atlantic SSTs and therefore be driven, at least in part, by the AMO.

Additionally, recent research suggests that Gulf of Maine seawater temperatures may be influenced by variability in AMOC strength. Zhang (2008) used output from an ocean-atmosphere coupled model to show that the path of the Gulf Stream, as identified by subsurface temperatures, was highly correlated to AMOC variability in a millennium control integration. The model results showed that the path of the Gulf Stream shifts to the south (north) with increased (decreased) strength of AMOC. These results were opposite to those presented by de Coëtlogon et al. (2006), who found a more northerly (southerly) path of the Gulf Stream with increased (decreased) AMOC strength using hindcast general circulation models. Joyce and Zhang (2010) compared observational data to the modeling output used by Zhang (2008) to demonstrate that this model was accurate in demonstrating the relationship between the path of the Gulf Stream and AMOC strength and that the correlation found by de Coëtlogon et al. (2006) was not reflected in observational data. This correlation between the path of the Gulf Stream and AMOC strength leads to a dipole temperature correlation with AMOC strength: AMOC strength has a positive correlation with seawater temperature south of Greenland but a negative correlation with seawater temperatures along the east coast of North America as warm waters move to the south with the shifting path of the Gulf Stream. Dima and Lohmann (2010) found a similar dipole correlation pattern when they looked at global SST data using empirical orthogonal function analysis to identify modes of climate variability. The authors found temperature anomalies to the south of Greenland, attributed to changes in AMOC strength, have the opposite sign to those found along the east coast of North America.

Therefore, several different North Atlantic oceanic and atmospheric climate modes have been implicated in the variability of Gulf of Maine hydrographic properties. However, the lack of a long-term instrumental record in the Gulf of Maine makes determining which of these climatic modes is the primary driver of Gulf of Maine seawater temperatures difficult. Temperature reconstructions that are continuous, precisely dated, annually resolved and multicentennial in length in the Gulf of Maine are therefore needed in order to better understand hydrographic influences and predict future climatic changes in the Gulf of Maine.

3.3.2 Recent changes observed in the Gulf of Maine

Recent changes seen in the Gulf of Maine further call into question the driver of hydrographic variability in the region and the future of Gulf of Maine climate. While the above review suggests that Gulf of Maine hydrographic variability may be closely related to the NAO, the relationship between the NAO and Gulf of Maine water properties appears to have changed in recent decades. Townsend et al. (2010) looked at nutrient data from the last 50 years and found that nutrient concentrations at depth have changed since the 1970s. These changes cannot be fully explained by variations in slope water related to changes in the NAO. Instead, the authors suggest that increased melting in the Arctic has led to increased buoyancy driven transport of the inner limb of the Labrador Current, leading to an increase in shelf water flowing into the Gulf of Maine and a subsequent decrease in slope water. Mountain (2012) also found that the NAO mode seemed to have less of an effect on hydrographic variability in the Gulf of Maine in recent decades. The author looked at temperature and salinity data to infer the percent of slope water comprised of LSW in the Gulf of Maine from 1960 to present and found a significantly smaller correlation between this percentage and the NAO after 1990. The lack of a correlation between the NAO and Gulf of Maine water temperatures is also seen in 2012, where surface temperatures reached record highs according to some instrumental data (Mills et al., 2013). Based on the formerly defined relationship between the NAO and Gulf of Maine water temperatures, a NAO high would be expected in 2010, two years prior to this record warming. Instead, the lowest NAO in the instrumental record occurred during that year (Osborn, 2011).

In addition to potential changes in drivers of Gulf of Maine hydrographic variability, some researchers have also suggested that Gulf of Maine SSTs have been drastically increasing recently. Satellite data suggest that that Gulf of Maine has been warming at a rate of 0.026°C/yr since 1982 and 0.26°C/yr since 2004, faster than 99% of the global ocean (Mills et al., 2013; Pershing et al., 2014). However, short-term monitoring stations within the Gulf of Maine do not corroborate the rapidity of this warming (D. Townsend, personal communication). Additionally, it is important to note that these findings have yet to be published in a peer-reviewed journal. The lack of long-term instrumental records in the Gulf of Maine makes it difficult to determine how much of this warming, if deemed reliable, is outside the natural variability of Gulf of Maine climate. Similarly, changes in drivers of Gulf of Maine hydrographic variability can not be accurately assessed as a complete understanding of what influences Gulf of Maine hydrographic variability is difficult without longer instrumental records. Therefore, in order to determine to what extent anthropogenic climate change is affecting the recent hydrographic changes seen in the Gulf of Maine, a longer record of hydrographic variability in the region is needed. This research seeks to provide such a record using oxygen isotopes from *Arctica islandica* shells.

3.3.3 *Arctica islandica* as a climate proxy

Arctica islandica (ocean quahog) is a marine bivalve mollusc and the longest-living, non-colonial animal currently known, with a lifespan of 375-507 years (Butler et al., 2013; Thompson et al., 1980; Wanamaker et al., 2008*b*). The longevity of this species makes *A. islandica* an ideal climate proxy as one specimen can provide a centuries-long continuous record of climate variability. *A. islandica* have a broad modern-day habitat range in the North Atlantic. The species is found as far south as Cape Hatteras on the east coast of North America and at least as far north as northern Scandanavia in the Arctic Ocean (Dahlgren et al., 2000). *A. islandica* have been found from shallow waters down to 500 meters depth (Nicol, 1951). This broad range in distribution, both in terms of latitude and depth, make *A. islandica* an ideal proxy for recording climatic changes throughout the North Atlantic.

The aragonitic *A. islandica* shell grows in annual increments, much like trees grow in annual rings (Jones, 1980; Thompson et al., 1980). The width of these annual increments is a factor of environmental conditions during the given year, especially seawater temperature and nutrient concentration (Schöne et al., 2005; Wanamaker et al., 2008*b*, 2009; Witbaard et al., 1997, 1994). Consequently, shells growing in a similar geographic location will display a similar pattern of annual increment widths. Therefore, the dendrochronological technique of crossdating, wherein increment width patterns are matched amongst live-caught and fossil specimens to determine when the shells (or trees in the case of dendrochronology) lived, can be utilized.

A. islandica shells are a particularly useful proxy for determining seawater temperature as these shells are precipitated in oxygen isotopic equilibrium with seawater (Weidman et al., 1994), meaning that biological effects do not influence the isotopic composition in the shell. The oxygen isotopic values measured in *A. islandica* shells are therefore only a factor of the temperature and oxygen isotopic composition of the seawater in which the shells were precipitated. By measuring oxygen isotopic values in the individual annual increments of *A. islandica* shells, seawater temperatures can be reconstructed in annual resolution. This thesis presents such a reconstruction for the Gulf of Maine.

3.4 Methods

3.4.1 Shell collection

Collection of both live-caught and fossil *A. islandica* shells occurred in June, 2010, June 2011, September 2012 and June 2014 at a depth of ~38 meters east of Seguin Island in the western Gulf of Maine (43.707060°, −69.756173°). Collection occurred on the fishing vessel *Nothin' Serious III* using a steel towing dredge. These collection trips produced a total of approximately 315 live-caught and 175 fossil shells. Shells were shipped to the Stable Isotope Laboratory (SIL) at Iowa State University in Ames, Iowa. Each shell was measured and weighed and notes were taken as to the biological condition of the shells.

3.4.2 Shell processing and dating

Shells were processed for analysis using similar techniques to those described by others (Butler et al., 2009; Scourse et al., 2006). Using a Gryphon diamond bladed saw, a 4 cm section was cut from the shell along the axis of maximum growth

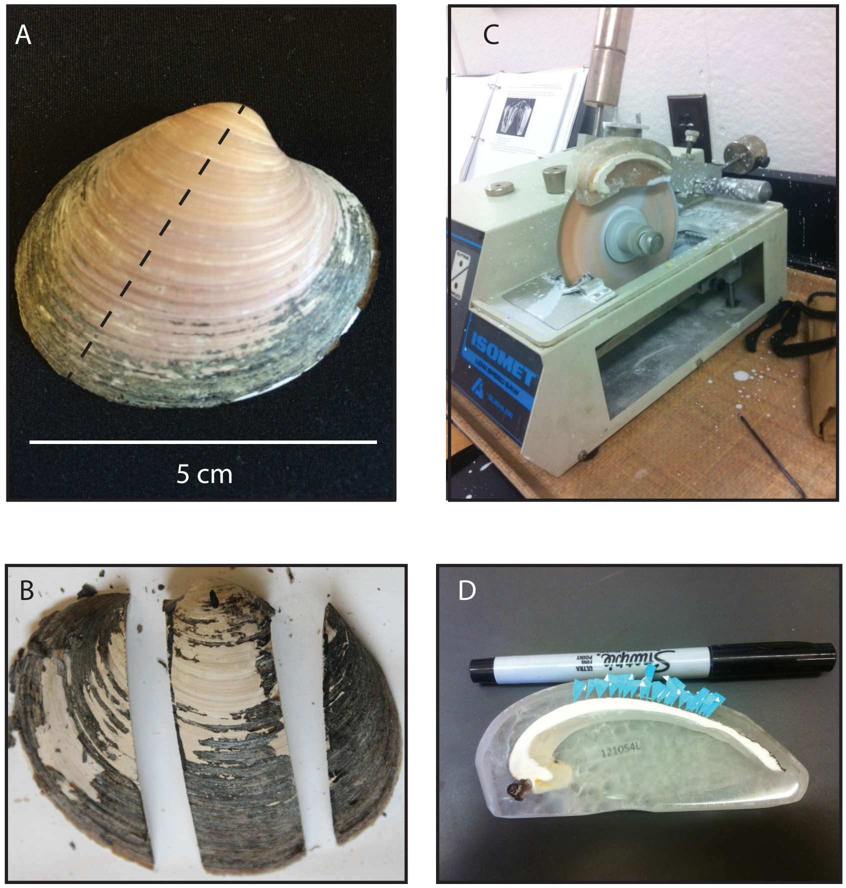

Figure 3.3. Images of select shell processing steps. (A) The right valve of an *A. islandica* shell. The dashed line marks the axis of maximum growth along which the shell will be sectioned after blocked in epoxy. (B) The 4 cm shell section (middle) containing the axis of maximum growth to be blocked in epoxy. (C) A shell section blocked in epoxy is cut in half using the Buelher IsoMet low-speed saw. (D) The resulting blocked shell cross-section. The first several annual increments on this shell are marked with teal tape.

(Figure 3.3A and B). When possible, the left valve of the shell was used in order to maximize hinge material present. This section of shell was then placed in a mold, which was subsequently filled with a Buelher Epoxicure resin and hardener. Once the epoxy had hardened, the epoxy block containing the shell was sectioned in half using a Buelher IsoMet low-speed saw, resulting in two blocks, each containing a cross-section of the shell along the maximum axis of growth (Figure 3.3C and D). The blocks were polished on a twin platen Buelher MetaServe 250 grinder-polisher system using a progressively fining grit from 120 to 1200. One of the two blocks from each shell was reserved for isotope analysis. The other block was used to date the shell and for use in constructing an increment width index chronology ("master chronology").

The dating of the shells is described in detail elsewhere (Griffin, 2012). Briefly, the block reserved for dating was etched in hydrochloric acid before an acetate replicate peel of the surface of the shell was made. This enabled the shell surface to be more visible under a microscope and through a uEye camera and for individual annual increments to be measured using Bueller OmniMet software (v.9.5). Increments were measured perpendicular to growth lines and at the maximum width of the increment (Figure 3.4). Because *A. islandica* shells precipitate in annual increments in both the hinge and the margin, increments in both regions of the shell were measured and compared to ensure no measurement errors were made.

Increment width series were first detrended using a negative logarithmic curve to remove ontogeny related growth patterns before being initially compared to other series using the MATLAB script SHELLCORR (Butler et al., 2009; Scourse et al., 2006). To compare two increment width indices from either the margin and hinge of one shell or between two individual shells, a Pearson correlation coefficient was calculated between the two indices with a 21 year running window and at a variety of leads and lags. Comparing individual shells to shells already dated in this manner

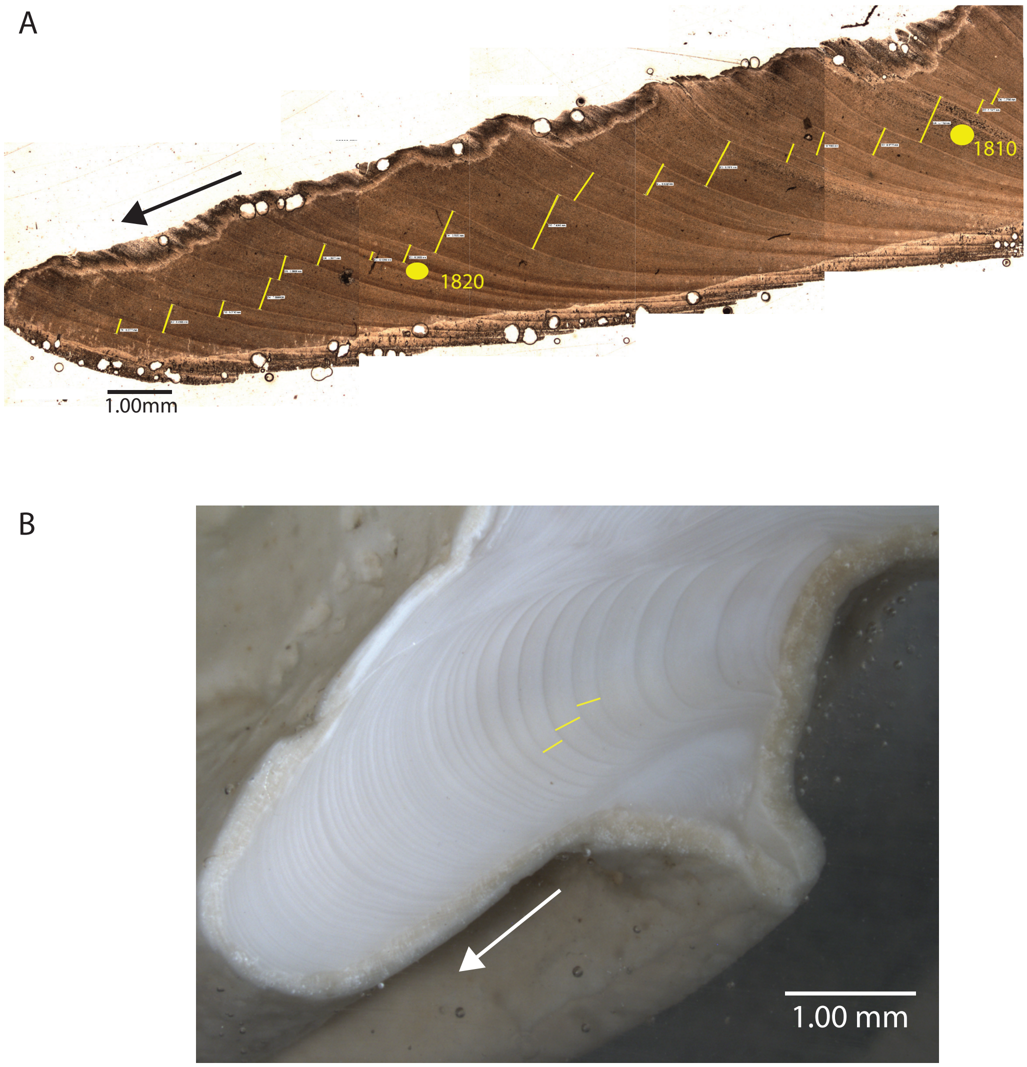

Figure 3.4. Images of annual increments in *Arctica islandica* shells. Yellow lines mark the width of select annual increments and show the orientation used for making measurements on the hinge and margin of shells. The arrows indicate the direction of the growth of the shell in both images. (A) An image, taken under a microscope, of the acetate peel of a shell that has been dated using crossdating techniques. The decadal increments are marked. (B) An image, taken under a microscope, of the hinge of a shell in an epoxy block under reflected light.

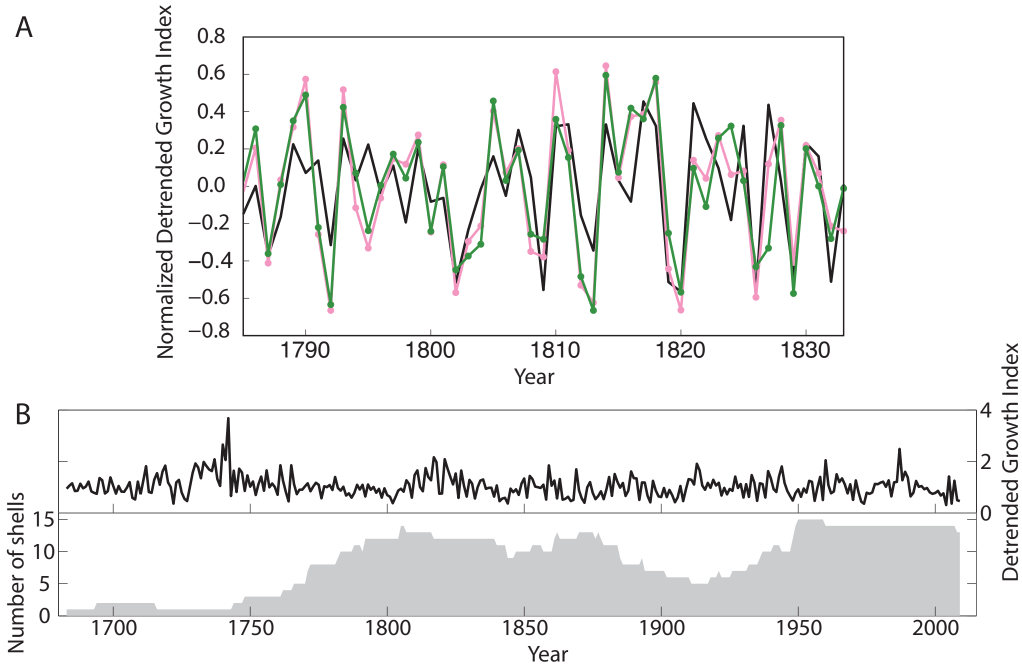

Figure 3.5. Examples of growth series for Gulf of Maine *Arctica islandica* shells, including the Gulf of Maine master chronology. (A) An example of SHELLCORR output showing the detrended grow index of the master chronology (black) and closely correlated growth index of the hinge (pink) and margin (green) of an *A. islandica* shell. (B) The master growth series for Seguin Island (top panel) and the number of shells in each part of the series (bottom panel; counts the margin and hinge of one specimen as two separate shells). Because of the small number of shells in the series before 1760, this series is not considered a master chronology before this time but instead a growth series.

allowed for errors in the measurement of annual increments of live-caught shells to be corrected. Additionally, this method enabled fossil shells to be dated by matching the increment width index to already dated shells in the chronology (Figure 3.5A). Fossil shells dated in this manner were first radiocarbon dated at the Woods Hole Oceanographic Institute in order to determine roughly when the specimen lived before definitive dates were found using the technique described above, termed crossdating. The final chronology was built using the software programs COFECHA, to statistically analyze the chronology and detect any errors (Grissino-Mayer, 2001;

Holmes, 1983), and ARSTAN (Cook, 1985), to detrend individual increment width indices and compile the final chronology (Figure 3.5B).

3.4.3 Oxygen Isotope Analysis

Once dated, the annual increments along the margin were milled using a New Wave MicroMill and a 80 μm carbide drilling bit (Figure 3.6A and B). Using software specific to the micromill, the path, number of passes and depth per pass could all be specified. The path on which the increments were milled varied during the processing as the best optimal path was sought to obtain oxygen isotopes from the full annual increment and not create a bias towards any one part of the increment (and therefore any one part of the year). Shells milled during the summer of 2014 were primarily milled perpendicular to the growth bands while those milled during the winter of 2015 were primarily milled parallel to the margin (Figure 3.6C). The milling technique was additionally changed in the winter of 2015 to further diminish bias by milling away shell material from the previous increment so that the milling path could be extended into the previous increment (Figure 3.6D). This change in milling technique was done to limit the bias evoked by the shape of the milling bit so that the milled path sat flush against the growth band at the beginning of the increment without excluding any one part of the annual increment at the start of the milled path (pink triangles in Figures 3.6C and D indicate those areas of the milled path excluded from the sample due to the shape of the drilling bit). The possible effects that these changes in milling technique had on isotope measurements is discussed in Section 3.5.1.

The number of passes for each increment ranged from 1 to 25 with the depth per path ranging from 50-100 μm. Changes to these two parameters were made depending on the width of the increment so that approximately 0.250-0.300 mg of carbonate powder were obtained from each sample. Samples were then collected

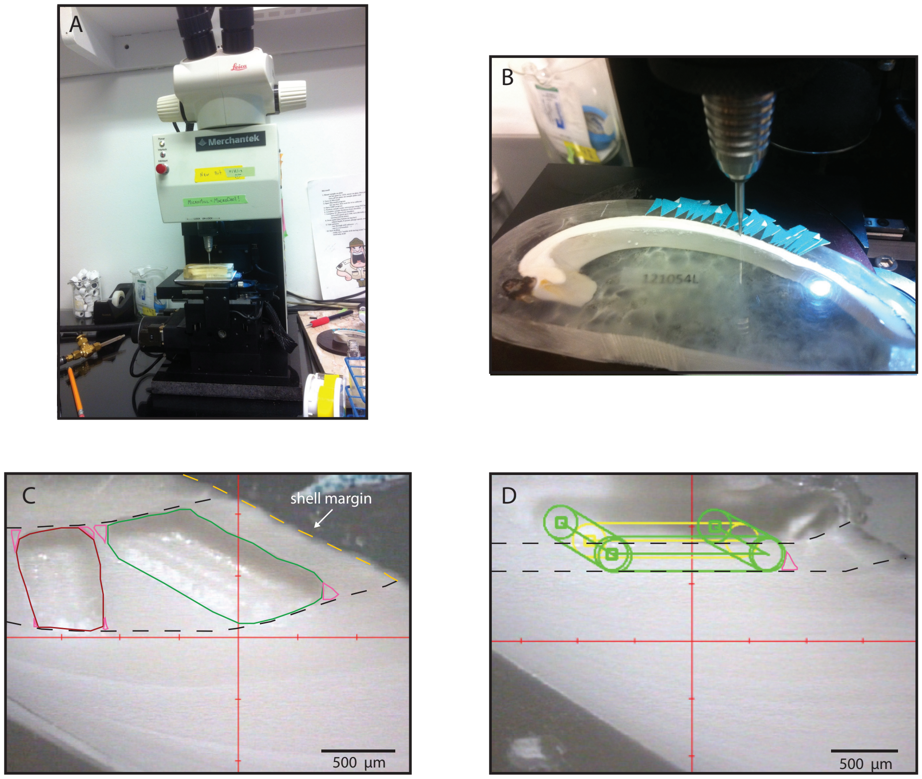

Figure 3.6. Images of the milling process for extracting carbonate powder from *A. islandica* shells for oxygen isotope analysis. (A) The New Wave MicroMill. (B) Drilling an increment of the shell. (C) Example of the two different paths used to mill the increments. The previously milled section outlined in red is an example of the milling path perpendicular to the annual growth increment (black dashed lines) used primarily for shells milled during the summer of 2014. The previously milled section outlined in green is an example of a milling path parallel to the shell margin (yellow dashed line) showing the milling pattern used primarily for shells milled during the winter of 2015. (D) Milling paths of an increment (bordered by black dashed lines) that go into the previously milled increment to avoid bias in the beginning of the increment, used primarily for those shells milled during the winter of 2015 (see text for details). For both (C) and (D), the pink triangles outline the part of the increment not milled due to the shape of the milling bit and thus the source of the bias in the resulting sample.

using a scalpel and razor blade, placed in 40 mL Exetainer vials and weighed. If the sample was too light, more shell material was milled if possible. If the sample was too heavy (much above 0.4 mg), the sample was split into two different samples. The resulting isotopic values were then averaged to produce one annual value based on the weight of each sample.

Before analysis, the samples were placed in a muffle furnace set at 40°C for at least 12 hours to remove any moisture. The vials were then capped and flushed with helium gas to remove atmospheric gases. The vials were subsequently injected with 100 μL of 95% phosphoric acid and the reaction was allowed to occur for 16-18 hours before the resulting gas was analyzed in the mass spectrometer. The mass spectrometer used was a ThermoFinnigan Delta Plus XL continuous flow isotope ratio mass spectrometer (IRMS). Samples were transported to the mass spectrometer through a Gas Bench equipped with a CombiPal Autosampler. Two reference standards, NBS-18 and NBS-19, were used with a third, LSVEC, used in some of the runs (the LSVEC standard produced inconsistent measurements in some of the early runs and so was excluded from the regression correction for these measurements). At least one reference standard was used for every five samples. Isotopic values for samples were determined using regression based analysis of the reference standards. The combined uncertainty in the run (including both analytical uncertainty and average correction factor) ranged from ±.04‰ (VPDB) to ±.29‰ (data from the run with the highest uncertainty was later discarded, as discussed in Section 3.5.1). The average uncertainty was ±0.095‰ (VPDB).

3.4.4 Reconstructing seawater temperatures using oxygen isotopes

Weidman et al. (1994) showed that *A. islandica* shells precipitate in isotopic equilibrium with seawater. The authors showed that the relationship between the oxygen isotopic composition of *A. islandica* shells ($\delta^{18}O_c$), the oxygen isotopic composition of the seawater ($\delta^{18}O_w$) in which the shell precipitated and the temperature of that seawater could be described by the equation originally determined by Grossman and Ku (1986) and later modified to adjust for a change in reference standard:

$$T(°C) = 20.60 - 4.34 \times (\delta^{18}O_c - (\delta^{18}O_w - 0.27)) \tag{3.1}$$

Therefore, if the oxygen isotope value of the seawater in which the shell grew can be determined, seawater temperature can be reconstructed from oxygen isotope values measured in *A. islandica* shells. While there are no long-term records of $\delta^{18}O_w$ near Seguin Island where the *A. islandica* shells were collected, there are some instrumental records of salinity in the area. Because salinity and oxygen isotopes covary with changes in precipitation and evaporation (discussed in detail in Chapter 2 of this thesis), the instrumental salinity data can be used to find average seawater oxygen isotope values in the region where the shells grew using the coastal Gulf of Maine $\delta^{18}O_w$-salinity mixing line presented in Chapter 2 of this thesis:

$$\delta^{18}O_w = 0.2S - 9.0 \tag{3.2}$$

S is salinity. The salinity used for this temperature reconstruction was taken from an average of salinity in the western Gulf of Maine as recorded by Northeastern Regional Association of Coastal and Ocean Observing Systems (NERACOOS) real-time buoys E01 on the Central Maine Shelf (43.70°, −69.35°; ∼30 kilometers east of the shell collection site) and B01 on the western Gulf of Maine (43.18°, −70.42°; ∼80 kilometers southwest of the shell collection site; Figure 3.7; http://gyre.umeoce.maine.edu/buoyhome.php). These buoys have been operational since July 2001 and record a variety of ocean properties, including salinity and temperature, at various depths. As seen in Figure 3.7B, B01 and E01 show similar values and trends in salinity at 50 meters depth. This mean salinity averaged be-

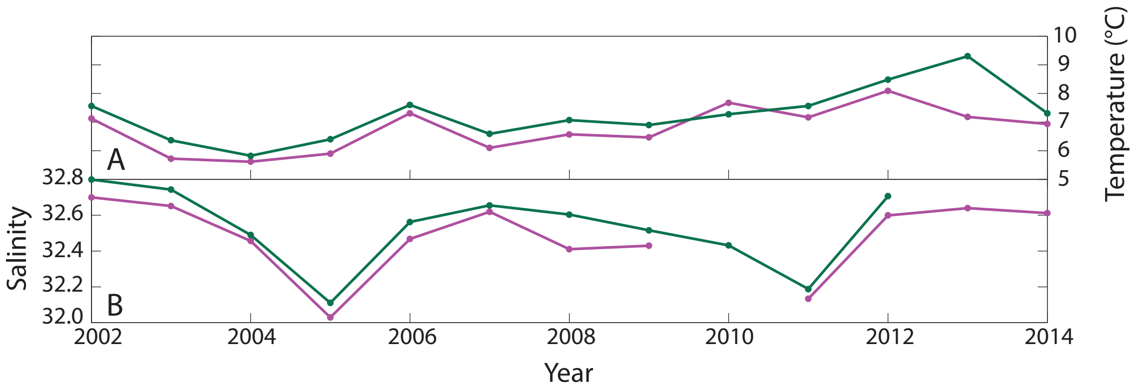

Figure 3.7. Temperature and salinity records from NERACOOS buoys at 50 meters depth in the Gulf of Maine. Temperature (A) and salinity (B) data are from buoys B01(green) and E01(purple; for the location of the buoys see text and Figure 3.2). Data from http://gyre.umeoce.maine.edu/buoyhome.php.

tween these two buoys at 50 meters depth from 2002-2014 was 32.5. This average salinity value is similar to that at 50 meters depths in the Bay of Fundy, where the Canadian Prince 5 station has recorded salinity since 1928. The average annual salinity from 1928-2013 at this location was 32.1 and ranged from 31.6 to 32.7. There are no statistically significant trends in this long-term salinity record (Wanamaker et al., 2008*a*) and therefore taking an average salinity from the data available is a reasonable approach.

The 50 meter depth mean salinity value averaged between buoys B01 and E01 was chosen for this reconstruction because the shell collection site lies between these two buoys (Figure 3.2) and is at approximately 38 meters depth. Therefore, this site location is likely primarily below the seasonal pycnocline and consequently more similar in salinity to waters at 50 meters depth than to waters at 20 meters depth (the next closest depth at which salinity measurements are taken on the buoy).

Equation 3.2 is reported with one significant figure after the decimal point due to the uncertainty associated with the salinity meter used. However, to calculate a precise average δ^{18}O$_w$, we use the equation with 4 significant figures after the decimal point:

$$\delta^{18}O_w = 0.2459S - 9.0374 \tag{3.3}$$

Using this equation and an average salinity of 32.5, an average δ^{18}O$_w$ of −1.0‰ is calculated.

3.5 Results

3.5.1 Analysis of data quality

Before specific oxygen isotope data is presented and discussed, it is necessary to assess the quality of the oxygen isotope data measured in Gulf of Maine *A. islandica* shells. Whenever possible, an attempt was made to make oxygen isotope measurements on multiple shells for any given year in order to verify that the oxygen isotope data measured in each shell were representative of the larger population and were therefore a reflection of environmental conditions (seawater temperature and δ^{18}O$_w$). While this replication produced good correlation in oxygen isotope values between shells for most of the time series, the replication was largely unsuccessful for several shells that lived after approximately 1915, with an offset of up to ∼10‰ (Figure 3.8) and an average standard deviation of 0.73 in a given year. Data obtained from increments dated before 1915 had an average standard deviation of 0.23 in a given year. It is important to note that some years before 1915 have large standard deviations in isotopic value and, conversely, some years after 1915 have small standard deviations in isotopic values and therefore good replication. However, because years after 1915 tended to have much larger ranges in δ^{18}O$_c$ values, it was decided that all samples after this date should be excluded from final analysis until a better understanding of the causes for this poor replication was gained.

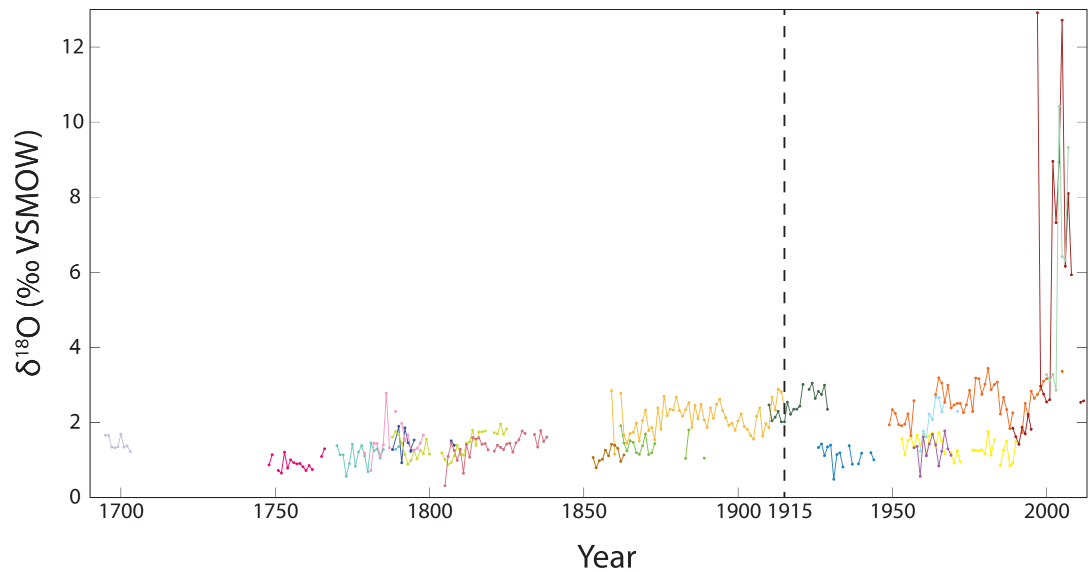

Figure 3.8. Oxygen isotope time series from 1695-2012. The dashed line at 1915 marks the point in the time series after which large variations in $\delta^{18}O_c$ for a given year appear in the data.

The first potential explanation for the offsets in oxygen isotope values found after 1915 is possible differences in habitat conditions for the individual organisms. For example, despite the fact that the specimens were all collected in proximity to each other and therefore most likely experienced similar environmental conditions during their lifetimes, it is certainly possible that individuals may have lived in an area affected by a microclimate (in a depression, on a ledge etc.) that tended to be colder or warmer than the surrounding area. There is no way of determining whether this is the case. However, it is unlikely that microclimates explain the full offset seen in the oxygen isotope data. Lab preparation and/or mass spectrometer run differences are therefore likely causing this offset in oxygen isotope values. Potential reasons are discussed below.

The relationship between various aspects of lab preparation and oxygen isotope value were assessed (Figure 3.9). Three key aspects of lab preparation were analyzed: weight of the carbonate sample, total depth milled into the shell for each sample and

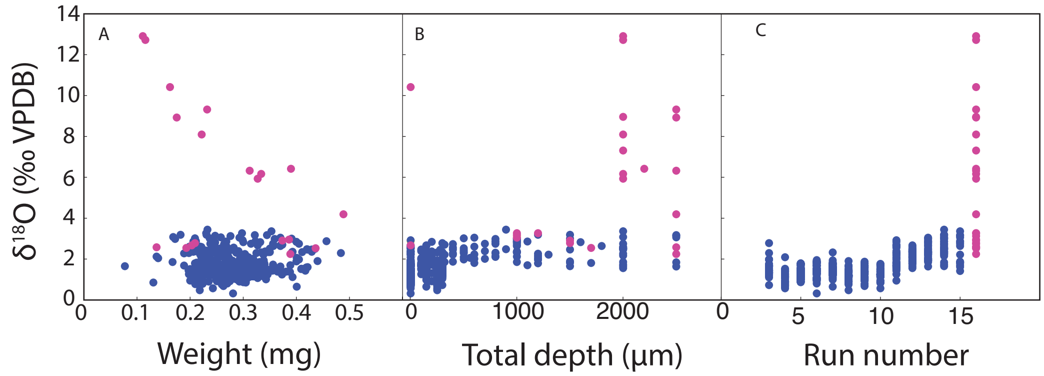

Figure 3.9. Plot of $\delta^{18}O_c$ versus various changes in sample preparation. Sample lab preparation variables considered include weight of the carbonate sample (A), total depth drilled in the shell to obtain the carbonate sample (B), and the number of the run in which the sample was included for mass spectrometer analysis (C). Each run corresponds to a different date of oxygen isotope analysis. Runs 1-10 were of samples milled in the summer of 2014. Runs 11-16 were of samples milled in the winter of 2015. Pink indicates samples from run 16 to highlight the significant number of outliers in this run.

the date that the sample was run through the mass spectrometer. Sample weight was assessed in order to determine if the mass spectrometer produced different oxygen isotope readings based on the amount of sample present. Total depth milled was assessed in order to determine if the heat from the drill bit, which presumably would increase with depth as the drill would be operating for longer periods of time, affected the $\delta^{18}O_c$. The date that the sample was analyzed was assessed to determine whether contamination, including from water vapor in the mass spectrometer or bad standards within the run et cetera affected the oxygen isotope composition. Student t-tests were performed on the data to assess the association between these three processing variables and the isotopic value measured.

Including all isotopic data, there was no statistically significant association between total depth milled and isotopic value ($p>0.05$). However, there was a statistically significant association between the isotopic value and the weight of the sample ($p<0.05$). Further analysis revealed that this association became statistically insignificant ($p>0.05$) when samples from run 16 (analyzed March 5, 2015) were removed. Samples in this run were measured to have isotopic values far outside the range of values expected for natural marine environments (as enriched as 12.9‰ which would result in a water temperature of around $-41°C$). Why this particular run had an association with sample weight while other runs did not is unclear. It is likely that some other factor contributed to the extreme values seen in this run, including possible contamination in the mass spectrometer.

Finally, statistical analysis revealed that there was also an association between run date and the isotopic values of the sample, even with run 16 excluded. Specifically, samples tended to have more enriched isotopic values if milled and run in the winter of 2015 as opposed to the summer of 2014. This is most likely due to the fact that, by chance, the specific shells milled during the winter of 2015 likely lived during colder periods (resulting in more enriched $\delta^{18}O_c$) than those milled and analyzed during the summer of 2014. However, this trend is also seen in shells that formed during the same time period: those milled in the winter had more enriched oxygen isotope values than those milled during the summer. As noted in Section 3.5.1, the milling technique did change from those shells milled in the summer of 2014 to those shells milled in the winter of 2015. One possible consequence of this change in milling technique is that the sample milled from an individual increment was no longer biased towards the middle of the growing season (the case for increments milled using the summer 2014 milling technique because the increment path was rounded on both sides of the increment; see Figure 3.6C and D for visual depiction). Instead, the sample milled using this technique was biased towards both the beginning and the middle of the growing season so that only the end of the growing year was not fully included in the sample. While eliminating as much bias as possible is generally desired and thus the reason for the change in milling technique, changing the milling technique so that only the end of growing year, which is September and October when the waters are generally the warmest, is not fully

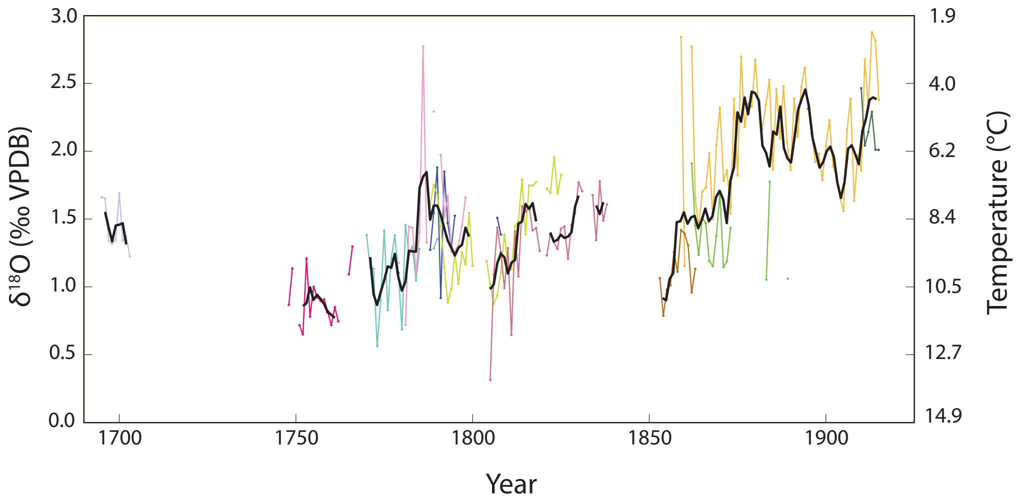

Figure 3.10. Oxygen isotope and derived temperature time series from 1695-1915. Time series of oxygen isotopes measured in precisely dated *Arctica islandica* shells collected off of Seguin Island in the Gulf of Maine (left axis). Conversion to seawater temperatures using the coastal Gulf of Maine mixing line and an average salinity of 32.5 (see text for details; right axis). The different colors signify individual shells. The black line is a three-year running mean.

included may result in $\delta^{18}O_c$ measurements that indicate an annual average temperature that may be slightly colder than the actual annual temperature. However, more analysis of milling techniques needs to be done in order to assess whether this change in technique could actually make a noticeable difference in isotopic value. It is unlikely that such a change would create the extent of the offset seen in the data.

Therefore, definitive reasons for the offset seen in the oxygen isotope data after 1915 are not known for certain at this time. More work needs to be done in order to assess other possible causes for these offsets and address any issues in milling technique, preparation of the sample et cetera that may arise from this assessment. The data analysis and discussion presented below will only consider data from increments dated from 1695-1915. We are confident in this data due to the general success of replication for this time period.

3.5.2 Oxygen isotope and temperature time series from 1695-1915

The annually resolved $\delta^{18}O_c$ data measured in Gulf of Maine *A. islandica* shell increments dated from 1695-1915 are presented in Figure 3.10. The oxygen isotope record extends from 1695 to 1915 with significant gaps in the record from 1704-1747 and 1839-1852 due to lack of wide enough annual increments for milling purposes during these time periods. Other than these two instances, there are no periods in the record of longer than four years with no data. $\delta^{18}O_c$ values range from 0.31‰ to 2.87‰ and oscillate on annual and multidecadal time scales.

Using an average $\delta^{18}O_w$ of -1.0 (calculated in Section 3.4.4) and Equation 3.1, temperature values were calculated from the oxygen isotope data. The reconstruction of temperatures in the Gulf of Maine at ~38 meters depth is presented along with the isotope data in Figure 3.10. Reconstructed temperatures range from 2.4°C to 13.5°C. These temperatures are calculated assuming that $\delta^{18}O_w$ remains constant throughout the entirety of the isotope time series. While this is obviously a potentially unrealistic assumption, a lack of $\delta^{18}O_w$ data or salinity records in this area make it necessary. This temperature reconstruction indicates that average annual water temperatures at ~38 meters depth varied by up to ~11°C during the 220 years included in the reconstruction.

It is an informative exercise to assume (unrealistically) that seawater temperatures remain constant in the Gulf of Maine and to reconstruct changes in salinity from the oxygen isotope record presented here. This could be done by first rearranging equation 3.1 to solve for $\delta^{18}O_w$:

$$\delta^{18}O_w = \delta^{18}O_c - .23T(°C) - 4.48 \tag{3.4}$$

Holding the temperature constant at the 2002-2014 average temperature at 50 meters from NERACOOS buoys B01 and E01 (excluding years where more than

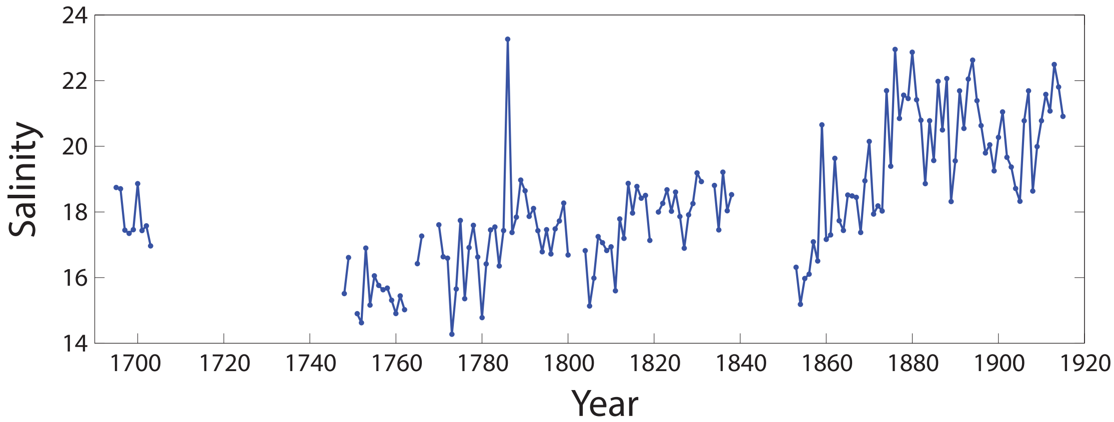

Figure 3.11. Reconstruction of salinity from average $\delta^{18}O_c$ values measured in *Arctica islandica* shells. See text for details.

two months worth of data were missing), 7.00°C, and using the oxygen isotope data measured in the *A. islandica* shells, the average $\delta^{18}O_w$ in a given year can be determined. Salinity at ~38 meters depth in the western Gulf of Maine can then be constructed by rearranging the coastal Gulf of Maine $\delta^{18}O_w$-salinity mixing line (equation 3.2) to solve for salinity:

$$Salinity = 4.3\delta^{18}O_c + 36.8 \qquad (3.5)$$

This salinity reconstruction is shown in Figure 3.11. Salinity values range from 14.3 to 23.3.

3.5.3 Correlating the Gulf of Maine $\delta^{18}O_c$ reconstruction with North Atlantic climate drivers

Below are summaries of the correlations found between the 1695-1915 Gulf of Maine oxygen isotope record presented in this thesis and instrumental and reconstructed records of North Atlantic climate drivers. The oxygen isotope record shows a statistically significant correlation with the AMO index during the month of April with no lag between 1853-1915 ($r=-0.33$, $p<0.05$, $n=62$). This index was defined as the SST anomaly (from the National Climatic Data Center's Extended Reconstructed Sea Surface Temperature - ERSST- dataset; Smith et al., 2008) for the North Atlantic (here defined as 25°-60°N, 7°-75°W) after subtracting the regression of the North Atlantic SSTs onto the global temperature average to get temperature changes specifically related to changes in the North Atlantic (van Oldenborgh et al., 2009). A negative correlation is expected since oxygen isotopes are inversely related to seawater temperatures.

The oxygen isotope record presented here did not have any statistically significant correlation with the instrumental record of the winter NAO index (December-March; based on sea level pressure measurements from Iceland and Gibraltar; Jones et al., 1997). Additionally, there was no correlation found between the oxygen isotope record and reconstructions of the NAO from Trouet et al. (2009).

The association between the oxygen isotope data and instrumental records of SSTs from 1854-1912 (the years for which SST data were available) was assessed. A three-year running average was used for each dataset based on the approximate flush time of the Gulf of Maine. The SST data used was from the ERSST dataset (v3b; v3 is described in Smith et al., 2008. V3b is similar to v3 but does not use satellite data; http://www.ncdc.noaa.gov/data-access/marineocean-data/extended-reconstructed-sea-surface-temperature-ersst-v3b). The correlation analysis used the assumption that the growth increments in the *A. islandica* shells begin growing in November (while the exact time that a new annual growth increment starts growing varies by location, increments tend to start growing in late Fall).There is a strong negative correlation between the oxygen isotope record and instrumental SSTs in the Gulf of Maine and surrounding western North Atlantic for September-January and particularly in November ($r>-0.5$, $p<0.05$; a correlation also exists using the unsmoothed data but it is not quite as strong; Figure 3.12A).

There is also a strong positive correlation between the oxygen isotope record and SSTs in the Labrador Sea and subpolar gyre region of the North Atlantic, again

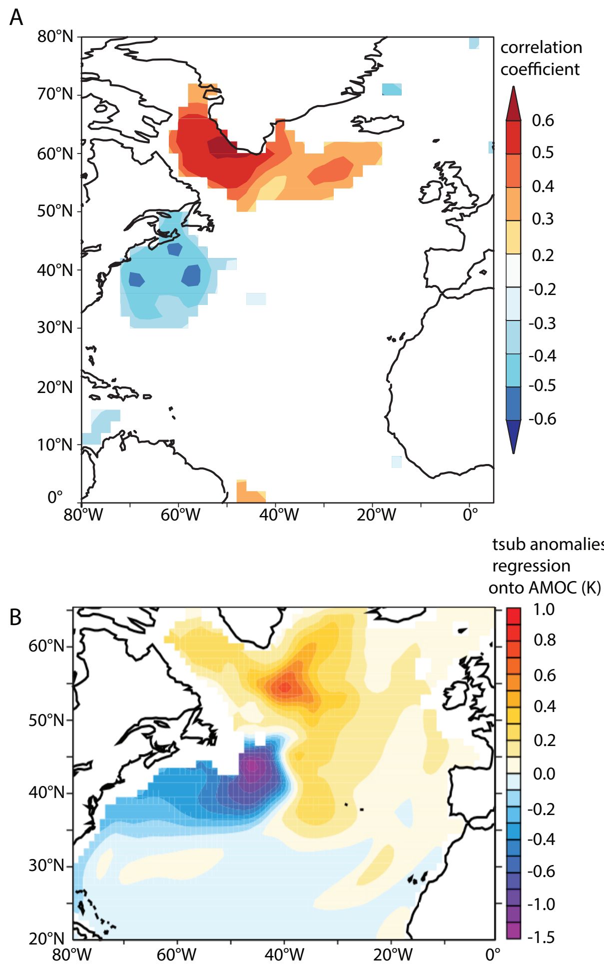

Figure 3.12. Maps of the North Atlantic demonstrating the potential link between Gulf of Maine hydrographic variability and AMOC strength. (A) The correlation between oxygen isotope values measured in *Arctica islandica* shells collected in the Gulf of Maine and November sea surface temperatures (SSTs) in the North Atlantic for the years 1854-1912. SST data are from the Extended Reconstructed Sea Surface Temperature (ERSST) dataset (v3b; http://www.ncdc.noaa.gov/data-access/marineocean-data/extended-reconstructed-sea-surface-temperature-ersst-v3b). A 3 year running-average was first applied to the oxygen isotope data. (B) Modeling results from Zhang (2008) of the regression of subsurface temperature anomalies on Atlantic meridional overturning circulation (AMOC). Warm colors indicate a positive association between AMOC strength and subsurface temperatures. Cool colors indicate a negative association between AMOC strength and subsurface temperatures. Modeling done using a fully-coupled ocean-atmosphere model, GFDL CM2.1. Figure from Zhang (2008).

particularly during the month of November ($r>0.6$, $p<0.05$; Figure 3.12A). This correlation suggests that there is an inverse association between seawater temperatures in the Labrador Sea/subpolar gyre regions and those in the Gulf of Maine.

3.6 Discussion

3.6.1 Validating the $\delta^{18}O_c$ time series as a record of seawater temperature variability in the Gulf of Maine

As in all paleoclimate reconstructions, the calibration of the temperature record derived from oxygen isotope values presented here with an instrumental record is an important check on the validity of the $\delta^{18}O_c$ as a recorder of seawater temperatures. Unfortunately, very few long-term instrumental records exist in the area. The Boothbay Harbor Environmental Monitoring Station temperature record dates back to 1905 but as discussed in detail in Chapter 1 of this thesis, that record has some sampling inconsistencies and does not necessarily accurately reflect temperature fluctuations in the greater Gulf of Maine (Drinkwater and Petrie, 2011). Additionally, if this record were used, there would only be 10 years worth of overlap between the instrumental record and the reconstructed temperature record. Therefore, it seems unwise to use this record to validate our temperature reconstruction. The only other instrumental record available in this area is the record from the NERACOOS buoys discussed in Section 3.4.4. Unfortunately, these buoys were only deployed in 2001. We do not yet have any valid oxygen isotope data for this time period (see Section 3.5.1 for explanation). Therefore, there is currently no means by which to test the validity of our temperature reconstruction. This work will certainly need to be done in the future.

However, several studies, including in the Gulf of Maine, have shown the legitimacy of using oxygen isotopes from *A. islandica* shells to reconstruct water temperatures (Wanamaker et al., 2008*a*; Weidman et al., 1994). Wanamaker et al. (2008*a*) found a strong negative correlation between oxygen isotopes measured in an *A. islandica* shell collected at 30 meters depth off of Seguin Island and the Boothbay Harbor SST record ($r = -.079$, $p < 0.0001$). The authors reconstructed seawater temperatures from these oxygen isotope values using salinity values obtained from 50 meters depth at the Prince 5 Station in the Bay of Fundy and the $\delta^{18}O_w$-salinity relationship found for Georges Bank and the Northeast Channel by Houghton and Fairbanks (2001). The Boothbay Harbor annual SST record had a strong correlation with these reconstructed seawater temperatures ($r = 0.71$, $p < 0.0001$). Seasonal Boothbay Harbor SST averages all showed similar correlations to the oxygen isotope time series and were lower than the correlation with the annual average SSTs, suggesting that *A. islandica* in the Gulf of Maine grow at a constant rate throughout the year. The Boothbay Harbor SSTs and the reconstructed seawater temperatures from Wanamaker et al. (2008*a*) shared ~50% common variance. Salinity records from Prince 5 and the $\delta^{18}O_c$ from the shell shared ~7% common variance. While this is a promising sign that oxygen isotopes measured in *A. islandica* shells collected in the Gulf of Maine are primarily influenced by seawater temperatures and can therefore be used to accurately reconstruct these seawater temperatures, it is again important to keep in mind the limitations of the Boothbay Harbor record as discussed above and in Chapter 1. More work needs to be done to verify the validity of this proxy.

The below analysis will address both the oxygen isotope time series and seawater temperature reconstruction derived from this oxygen isotope data. It is important to remember that the oxygen isotope time series represents hydrographic variability in the system. Because this variability is most likely largely associated with changes in temperature, analysis of the temperature reconstruction is done in order to reach the most likely conclusions about hydrographic variability in the Gulf of Maine over the last 1000 years. However, the oxygen isotope data presented here likely also reflects some changes in salinity. If a constant temperature is assumed, the range of salinity values, 14.3 to 23.3, indicated by the $\delta^{18}O_c$ values measured in shells dated from 1695 to 1915 (see Section 3.5), are much lower in this area than would be expected based on instrumental records and natural ocean salinity ranges in general absent any direct freshwater contribution (unlikely at 38 meters depth). Therefore, the $\delta^{18}O_c$ presented here are certainly a function of temperature. However, the amount of variance in these values explained by changes in $\delta^{18}O_w$ (and consequently changes in salinity) can not be quantified at this time. Future work will look to reconstruct changes in salinity in the area by reconstructing temperature variability from annual increment widths of *A. islandica* shells.

The $\sim$11°C variance in temperature suggested in the oxygen isotope record is likely in part due to changes in salinity and therefore the temperature variance experienced in the Gulf of Maine is likely less than $\sim$11°C. However, it is safe to say that even with taking into account the fact that some of this variance is the result of changes in salinity and not water temperature, the variance in water temperature from 1695-1915 is still likely larger than the 6° temperature variation recorded in the Gulf of Maine over the last century by the Boothbay Harbor Environmental Monitoring Station.

3.6.2 One thousand years of hydrographic variability in the Gulf of Maine

It is particularly informative to look at the oxygen isotope and reconstructed seawater temperature record presented here in the context of the 1000 year Gulf of Maine oxygen isotope and seawater temperature reconstruction from Wanamaker et al. (2008*a*) (referred to in the remainder of this paper as the "Wanamaker reconstruction"; Figure 3.13). As described in the introduction to this thesis, Wanamaker

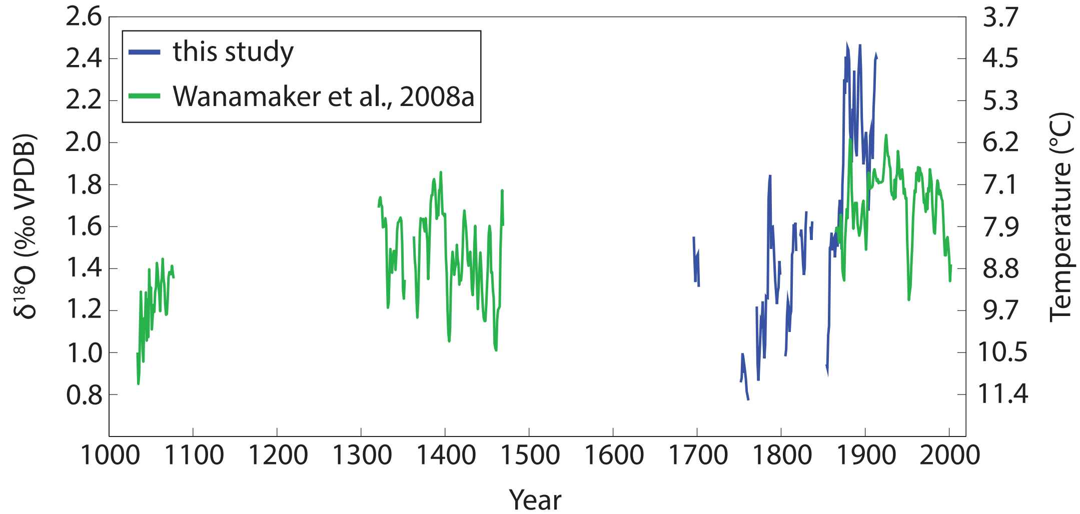

Figure 3.13. A 1000 year record of $\delta^{18}O_c$ measured in *Arctica islandica* shells collected in the Gulf of Maine. Both time series presented here are three year running averages. Data before 1695 are from shells that were radiocarbon dated.

et al. (2008*a*) used oxygen isotopes measured in 4 *A. islandica* shells collected in the western Gulf of Maine to reconstruct seawater temperatures in the region over the last millennium. This reconstruction found a $1-2$°C cooling in the Gulf of Maine over the last 1000 years.

The oxygen isotope and resulting seawater temperature reconstructions presented in this thesis fill in some of the gaps in the Wanamaker reconstruction, particularly during the climatologically important period at the end of the Little Ice Age (LIA; ∼1850 AD). These data imply warming waters from 1695-1761 before temperatures begin to cool until the record ends in 1915. This reconstruction includes water temperatures both cooler and warmer than any seen in the Wanamaker reconstruction and suggests larger, centennial scale oscillations in Gulf of Maine hydrographic variability. This variability implies that the Gulf of Maine cooling suggested by the Wanamaker reconstruction may be an artifact of when during the period of this centennial scale hydrographic variability oscillation these shells were sampled. More data is needed to fill in the remaining gaps of this 1000 year reconstruction of Gulf of Maine hydrographic variability in order to determine the amplitude of this oscillation and whether any long-term trends not related to this oscillation are present in the Gulf of Maine over the last 1000 years.

Wanamaker et al. (2008*a*) suggested that the apparent cooling in the Gulf of Maine over the last 1000 years inferred from their seawater temperature reconstruction implies cooling or increased transport of the Labrador Current over the last millennium and the concurrent reduction in influence of the Gulf Stream on water properties in the Gulf of Maine. The new $\delta^{18}O_c$ data presented in this thesis suggest that the influence of these two major ocean current systems on Gulf of Maine hydrographic properties has not necessarily changed over the last 1000 years but has instead oscillated on centennial time-scales. These data indicate the Gulf Stream has increasingly more influence on Gulf of Maine hydrographic properties from 1695-1761, after which Gulf Stream influenced waters in the Gulf of Maine declined, replaced by waters carried by the Labrador Current. Temperature values calculated from oxygen isotope values measured in *A. islandica* shell increments dated to around 1760 indicate that water temperatures were similar to or warmer than water temperatures from the early part of the millennium derived in the Wanamaker reconstruction, again suggesting that the Gulf Stream's influence on hydrographic properties in the Gulf of Maine has not diminished over the past 1000 years but instead has alternated in dominance with the Labrador Current's influence. A more continuous reconstruction of seawater temperatures in the Gulf of Maine over the last 1000 years is needed before any millennial scale trends in ocean current influence on Gulf of Maine hydrographic properties can be assessed.

It is interesting to note the correlation between the oxygen isotope data presented in this thesis and that presented in the Wanamaker reconstruction during the period that the two records overlap (1864-1915). Oxygen isotope values show good similarity between the two records for the first half-decade. However, after that, oxygen isotopes from this study suggests further significant cooling in the Gulf of Maine while the data presented in the Wanamaker reconstruction do not suggest such a change in temperature. One reason for this discrepancy is likely due to the fact that the oxygen isotopes presented in the Wanamaker reconstruction come from a shell collected at 30 meters water depth while the oxygen isotope data presented here were measured in shells collected at ~38 meters depth. In this region of the Gulf of Maine today, it is likely that at least during parts of the year, the thermocline is somewhere between 30 and 38 meters water depth. Therefore, these two different depths may experience significantly different hydrographic regimes in the Gulf of Maine at different times of the year during modern times.

Because the two reconstructions overlap right at the end of the LIA, the fact that they are similar from 1865-1870 before diverging suggests possible changes in the thermocline at the end of the LIA. For example, it is possible that during the LIA, with which colder, stormier conditions are associated, the seasonal thermocline was below 38 meters water depth as the colder surface waters and windy conditions kept the water column mixed. As the Gulf of Maine emerged from the LIA and surface temperatures became warmer and less disturbed by wind, the seasonal thermocline may have decreased in depth to some point between 30 and 38 meters so that the shell used in the Wanamaker reconstruction experienced water conditions above the thermocline (generally warmer) and the shells used in the reconstruction presented in this paper experienced hydrographic conditions below the thermocline. A larger overlap in the two records is necessary in order to better test this theory.

A comparison between reconstructed water temperatures in the Gulf of Maine over the last 1000 years and water temperatures in the Gulf of Maine today indicates that the recent warming in the Gulf of Maine suggested by some (Mills et al., 2013; Pershing et al., 2014) is not outside the range of natural variability in the region. The reconstruction presented here suggests that waters have been warmer in the

Gulf of Maine than they are today due to the natural, centennial-scale oscillations in the climate system. A better understanding of the natural drivers of Gulf of Maine hydrographic variability (discussed in the next section) will allow a better interpretation of whether the warming noted recently (although, as stated elsewhere, not corroborated by all instrumental records) is in fact due to anthropogenic climate change or instead due to natural or anthropogenically influenced oscillations of the primary drivers of Gulf of Maine hydrographic variability.

3.6.3 Drivers of Gulf of Maine hydrographic variability

One of the primary reasons for reconstructing hydrographic variability in the Gulf of Maine is to determine the climate drivers in this region. Not only will this help in predicting future hydrographic conditions in the Gulf of Maine but this will also lead to a better understanding of larger, basin-wide regulators of ocean climate, knowledge which is crucial in predicting global climate changes in the future. As highlighted in the introduction, the NAO has been suggested to be one of the primary drivers of hydrographic variability in the Gulf of Maine. The fact that no statistically significant correlation exists between the oxygen isotope reconstruction presented here and the instrumental and/or reconstructed NAO index time series suggests that the correlations found between the NAO and seawater temperatures in the Gulf of Maine during the instrumental record may not be representative of the NAO's influence on Gulf of Maine hydrographic variability over longer time-scales. This analysis is further supported by the fact that the correlation between the NAO and instrumental records of Gulf of Maine seawater temperatures has changed in recent decades (Mountain, 2012; Townsend et al., 2010), as mentioned in Section 3.3.1. Clearly the relationship between the NAO and seawater temperatures in the Gulf of Maine is not robust. Other major drivers of hydrographic variability in the Gulf of Maine need to be addressed.

The $\delta^{18}O_c$ data presented here do suggest an association between the AMO and Gulf of Maine water temperatures. While the correlation between the $\delta^{18}O_c$ data and the AMO is not particularly strong and the dataset sample is quite small, this correlation does suggest that Gulf of Maine water temperatures are driven to some extent by oscillations in the water temperatures in the greater North Atlantic region. This association is important to consider when assessing the recent warming in the Gulf of Maine that some instrumental records have indicated (Fogarty et al., 2007; Mills et al., 2013; Pershing et al., 2014). The AMO has recently been in a positive phase, as indicated by recent positive SST anomalies in the North Atlantic region (Mann et al., 2009), and therefore some of the possible warming occurring in the Gulf of Maine could be related to this natural oscillation in SSTs in the broader North Atlantic and not the result of anthropogenic climate change.

The correlation between the oxygen isotope record presented in this thesis and instrumental records of SSTs in the broader North Atlantic (Figure 3.12A) suggests that the AMOC is a potential primary driver of hydrographic variability in the Gulf of Maine. The dipole pattern of the correlation between the Gulf of Maine oxygen isotope record and seawater temperatures in the North Atlantic strongly resembles the dipole temperature pattern suggested by several authors to be caused by the AMOC (see Section 3.3.1; Figure 3.12B; Dima and Lohmann, 2010; Joyce and Zhang, 2010; Zhang, 2008).

The oxygen isotope record presented here therefore suggests that Gulf of Maine waters may be primarily influenced by variability in AMOC strength. If this is the case, the reconstruction of hydrographic variability in the Gulf of Maine implies that AMOC strength has oscillated on multi-decadal and centennial time-scales in the past millennium. In particular, AMOC strength likely decreased from 1695-1761, moving the Gulf Stream path farther north, closer to the Gulf of Maine so that warm waters associated with the Gulf Stream had more of an influence on hydrographic variability in the region. From 1761 to at least 1915, AMOC strength increased, causing the Gulf Stream to move to the south, away from the Gulf of Maine, and allowing colder waters from the Labrador Current to dominate Gulf of Maine hydrographic properties.

This reconstruction of AMOC variability is similar to Lund et al. (2006)'s reconstructed Gulf Stream transport (a component of AMOC). The authors used $\delta^{18}O_c$ measured in foraminifera from sediment cores in the Florida Straights to show that transport was reduced during the LIA and decreased from 1550-1750 before increasing until at least 1950, similar to the patterns found in the record presented here (Figure 3.14). While the Lund et al. (2006) reconstruction has only centennial scale resolution, the fact that both reconstructions show the same general patterns is promising.

Similarly, Wanamaker et al. (2012) found reduced AMOC strength during the LIA using ΔR values measured in *A. islandica* shells collected off the north coast of Iceland. The authors found a dominance of older, Arctic derived waters during the LIA indicating a weaker AMOC. The influence of younger North Atlantic waters on the north coast of Iceland increased after 1940, suggesting increasing strength of the AMOC. While the timing of the increase in AMOC strength varies, the general pattern of decreased AMOC strength during the LIA and a rebound in AMOC strength after the LIA is similar to the reconstruction presented here.

However, the reconstruction presented here shows opposite trends to the recent Rahmstorf et al. (2015) AMOC reconstruction. These authors attributed the difference in temperature between the sea surface around the subpolar gyre region of the North Atlantic and the Northern Hemisphere to the AMOC and therefore were able to create a reconstruction of AMOC variability using reconstructed temperature data from Mann et al. (2008) and Mann et al. (2009), which is almost exclusively terrestrial in origin. While there are no particularly obvious trends in this AMOC

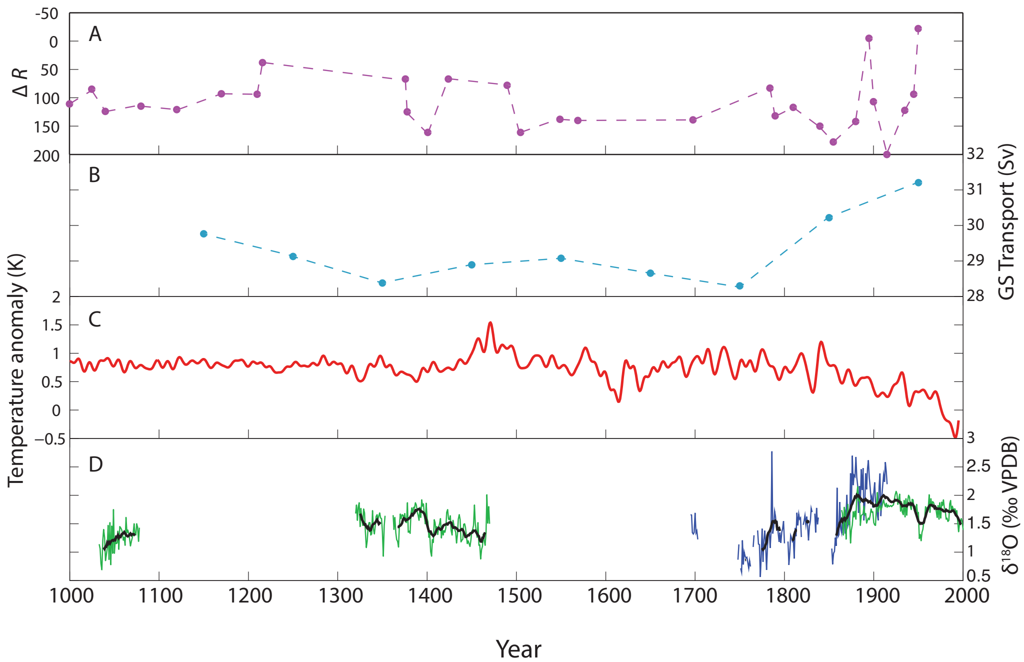

Figure 3.14. Time series' of AMOC reconstructions. (A) ΔR values from *Arctica islandica* shells from Wanamaker et al. (2012). More negative ΔR values suggest increased AMOC strength (note the inverted axis). (B) Reconstruction of Gulf Stream strength from Lund et al. (2006). (C) Reconstruction of the temperature anomaly calculated by subtracting reconstructed Northern Hemisphere temperature from North Atlantic subpolar gyre region reconstructed temperature. Rahmstorf et al. (2015) suggest that this reconstruction is an indication of AMOC strength variability. Data is decadally smoothed. (D) $\delta^{18}O_c$ values measured in *A. islandica* shells collected in the Gulf of Maine from this study (blue) and from Wanamaker et al. (2008*a*). The black line is a decadally smoothed average of the two data sets. In each panel, increased AMOC strength is up axis.

reconstruction from 1695-1850, the reconstruction indicates weakening after ~1850, which is opposite to the trends in AMOC strength noted above from this reconstruction and from those published by Lund et al. (2006) and Wanamaker et al. (2012) (Figure 3.14).

More research is needed in order to identify the causes of the discrepancies between these AMOC variability reconstructions. It is certainly possible that the Rahmstorf et al. (2015) reconstruction does not fully capture AMOC variability due to the fact that the proxy data used to infer marine temperatures are from terrestrial sources and therefore may not fully capture changes in marine climate. It is also possible that the authors' interpretation of what the difference in surface temperature between the North Atlantic subpolar gyre region and the Northern Hemisphere signals in terms of changes in AMOC variability is not correct. Alternatively, the interpretations of the other proposed AMOC variability reconstructions could be incorrect. With so few precisely dated, annually resolved AMOC reconstructions and no long-term instrumental records, it is difficult to fully understand the behavior, oscillations and influence of the AMOC on various regions of the North Atlantic and therefore to interpret the paleoclimate data suggested as proxy records of the AMOC. Multicentennial, continuous, precisely dated and annually resolved records are therefore crucial for interpreting the AMOC and should be prioritized in future paleoclimate work in order to allow for more accurate modeling and predictions of the AMOC and global climate in the future.

The possible correlation between seawater temperatures in the Gulf of Maine and AMOC strength is particularly important when predicting future climatic conditions in the Gulf of Maine because the AMOC is expected to slow with anthropogenic climate change (Gregory, 2005; Manabe et al., 1991; Ortega et al., 2011). As the Greenland Ice Sheet melts, North Atlantic SSTs increase and warmer air carries more moisture to the northern North Atlantic, waters in the North Atlantic will become less dense, decreasing deep water formation and leading to decreased AMOC strength. In fact, several analyses of AMOC strength suggests that it has already slowed (Bryden et al., 2005; Rahmstorf et al., 2015). Due to the likely negative correlation between AMOC strength and Gulf of Maine hydrographic variability, demonstrated by the oxygen isotope data presented in this thesis, a weaker AMOC with increasing global warming could mean much warmer waters in the Gulf of Maine in the future.

It is interesting to note the periods of the year where correlations between the oxygen isotope record and North Atlantic climate drivers exist. The reconstructed oxygen isotopes time series only correlates with the AMO (with a 0 month lag) during the month of April. However, the strongest correlation between basin-wide SSTs and the oxygen isotope record occur in the fall and early winter months, particularly in November, which is presumed to be the start of the growing year for *A. islandica* shells in the Gulf of Maine. One would assume that the strongest correlations would occur during the period of the year when the shell increments grew the fastest (as oxygen isotopes measured across the whole increment would be biased towards the months that have the most growth). However, since the AMO and North Atlantic SSTs have the highest correlations during different periods of the year, perhaps some other factor besides growth rate of the shell is involved. More research on the rate of shell growth in the Gulf of Maine as well as when exactly during the year the annual growth band is laid down is needed.

3.7 Conclusions

Understanding the natural hydrographic variability of the Gulf of Maine and the influences on that variability is crucial to understanding the climatic changes that are occurring in the Gulf of Maine presently and predicting what may happen in the future with increasing atmospheric greenhouse gases from anthropogenic activities. This thesis presents an annually resolved, absolutely dated, fairly continuous oxygen isotope time series and seawater temperature reconstruction from oxygen isotopes measured in *A. islandica* shells collected at ~38 meters water depth near Seguin Island in the western Gulf of Maine. This time series and reconstruction sheds new light on hydrographic variability in the Gulf of Maine. In particular, the time series reveals that hydrographic properties, presumably predominantly seawater temperature, have centennial scale oscillations that are of much larger amplitude than once thought. These oscillations suggests large fluctuations between the Gulf Stream and the Labrador Current as the dominant current system influencing Gulf of Maine water properties

Reconstructing these hydrographic oscillations in the Gulf of Maine contributes new insight into potential climate drivers in the region. While there was a statistically significant but minimal correlation between the oxygen isotope record in the Gulf of Maine and the AMO, the strong correlations between this record and the western North Atlantic SSTs (negative correlation) and the Labrador Sea/subpolar gyre region SSTs (positive correlation) in the fall and early winter months suggests that AMOC may be the primary driver of hydrographic variability in the Gulf of Maine. More research needs to be done to verify this connection between water temperatures in the Gulf of Maine and AMOC strength but these initial associations suggests oxygen isotope reconstructions from *A. islandica* shells in the Gulf of Maine could be used as an annually resolved, precisely dated marine proxy of AMOC variability. Such a proxy record is needed in order to better understand AMOC's influence on North Atlantic and global climate and how AMOC and related global climate, will change with increasing atmospheric greenhouse gases.

This large oscillations in hydrographic variability is significant when looking at the recent temperature trends in the Gulf of Maine mentioned in Section 3.3.2. As stated, several researchers have suggested, using primarily satellite data of Gulf of Maine SSTs, that the Gulf of Maine is warming faster than 99% of the world's oceans in recent years. While *in situ* instrumental data do no support this claim, the Boothbay Harbor Environmental Monitoring Station record does suggest warming since the 1970s. However, the temperature reconstruction presented here, along with the temperature reconstruction from Wanamaker et al. (2008*a*) suggests that the warming seen in the Gulf of Maine recently is not currently outside the realm of natural variability. In other words, it has been this warm and warmer in the Gulf of Maine in the past millennium, at least at ∼38 meters water depth. Therefore the suggested recent warming in the Gulf of Maine can not be unequivocally linked to anthropogenic climate change without additional evidence to suggest the cause for this warming. However, the apparent negative correlation between the AMOC strength and Gulf of Maine seawater temperatures reconstructed in this paper suggests that Gulf of Maine waters will warm in the future with the predicted decline in AMOC strength (Manabe et al., 1991).

Chapter 4
CONCLUSIONS

4.1 Predicting future climate change

The Intergovernmental Panel on Climate Change has stated that the earth, including the oceans, is "unequivocally" warming and that the warming is the result of anthropogenic activities (IPCC, 2013). However, it remains difficult to predict how the world's climate system will respond to future increasing greenhouse gases in the atmosphere. A large amount of this uncertainty stems from the abundance of unknowns associated with the world's climate drivers.

In the North Atlantic, which is known to significantly influence global climate (Levitus et al., 2000; Manabe and Stouffer, 1999*b*; Sabine et al., 2004; Visbeck, 2002), the primary drivers of climate are the North Atlantic Oscillation (NAO), the Atlantic Multidecadal Oscillation (AMO) and the Atlantic meridional overturning circulation (AMOC). The extent to which the influence and interactions of these climate regulators is understood is discussed in Chapter 1 of this thesis. As this summary suggests, there is still a lot of research that needs to be done on the influence that these climate drivers have on aspects of the North Atlantic climate and circulation and each other as well as on the origin of the oscillations seen in these climate drivers. Increased understanding of these climate modes is necessary both in order to better evaluate how future warming and increased atmospheric greenhouse gases will impact these climate drivers and consequently the earth's climate system but also how the natural oscillations in these climate drivers will affect the climate system and possibly lead to climatic changes not considered when simply predicting the climatic effect of increasing greenhouse gases.

There is a particularly significant amount of uncertainty associated with the AMOC, largely related to the difficulty in quantifying the AMOC resulting in sparse instrumental records. This lack of longterm instrumental data makes it necessary to turn to reconstructions of the AMOC in order to understand both the natural oscillations in the AMOC as well as how it might interact with the other North Atlantic climate drivers and the global climate system. Unfortunately, most of the AMOC reconstructions that do exist have multi-decadal to centennial scale resolution and dating errors associated with them (e.g. Lund et al., 2006; Wanamaker et al., 2012), making it impossible to understand AMOC variability on annual and multi-decadal time scales. Such high resolution is necessary in order to better predict what may happen to the climate system in the coming decades.

A recent AMOC reconstruction by Rahmstorf et al. (2015) offers decadal resolution and suggests that the AMOC is weaker now than it has been in the last 1000 years, a finding that the authors attribute to decreased density in North Atlantic waters from increased melting of the Greenland Ice Sheet. If true, this weakening of AMOC would have significant impacts on North Atlantic climate and could act as a negative feedback to the general global warming. However, as pointed out in Chapter 3 of this thesis, the reconstruction relies on a network of proxy data compiled by Mann et al. (2008) that includes very few climate reconstructions from marine proxies and therefore makes a significant number of assumptions when inferring ocean surface temperatures.

Clearly, annually resolved marine proxies of AMOC strength are needed. Such proxies which in addition have little dating error associated with them will provide invaluable insight into how the AMOC varies on a variety of time scales, including annual, and how the AMOC is associated with other North Atlantic climate drivers as well as how it may be related to climatic changes in the past. One such proxy, an annually resolved record of oxygen isotopes measured in precisely dated increments of *Arctica islandica* shells, is presented in this thesis.

4.2 Primary conclusions from this thesis

As detailed in the Chapter 1, modeling and observational data suggest that the strength of the AMOC is correlated with the path of the Gulf Stream. When AMOC increases in strength, the path of the Gulf Stream moves to the south (Joyce and Zhang, 2010; Zhang, 2008). Seawater temperatures in the Gulf of Maine, which are influenced by the warm waters associated with the Gulf Stream and therefore affected by the path of the Gulf Stream, are consequently likely associated with variability in AMOC strength. The Gulf of Maine is therefore a potentially ideal location to investigate annually resolved proxies for seawater temperature with the goal of reconstructing AMOC strength.

Chapter 2 of this thesis lays the groundwork for interpreting the oxygen isotopic record from *A. islandica* shells presented in Chapter 3 in terms of seawater temperature. In it, the δ^{18}O-salinity relationship of coastal Gulf of Maine waters is presented. Because the shells used as a proxy for seawater temperatures in this research were collected near the coast, the coastal mixing line presented in this chapter provides the most accurate estimate of average $\delta^{18}O_w$ from instrumental records of salinity in the region, an estimate which is necessary in order to calculate seawater temperature from δ^{18}O values measured in *A. islandica* shells.

Additionally, annual sampling of coastal Gulf of Maine waters reveals the seasonal influence of river runoff, likely primarily as a result of changes in river discharge rates. Decreased salinity and δ^{18}O values of coastal waters appear to result from local river runoff. $\delta^{18}O_w$ value become more uniform and more enriched during summer and fall months when river discharge is low, indicating that ocean water masses carried on coastal currents have more of an effect on coastal water composition during these seasons. Understanding modern hydrographic dynamics in Gulf of Maine waters through water sampling is necessary in order to interpret reconstructions of seawater properties in the Gulf of Maine.

Chapter 3 presents an annually resolved record from 1695-1915 of oxygen isotopes measured in *A. islandica* shells which were collected at ~38 meters water depth off of Seguin Island in the western Gulf of Maine. Using the $\delta^{18}O_w$-salinity mixing line presented in Chapter 2, this record is interpreted as a temperature record for the region. When combined with the Wanamaker et al. (2008*a*) isotope record for the Gulf of Maine, this reconstruction reveals large, centennial scale oscillations in Gulf of Maine waters, indicating that the Gulf of Maine has perhaps not cooled in the last 1000 years as previously thought (Wanamaker et al., 2008*a*). This reconstruction also indicates that the warming recently suggested for Gulf of Maine waters is not unprecedented in the last 300 years and that therefore caution needs to be taken when attributing this warming to anthropogenic activities as opposed to natural variability.

Promisingly, when compared to the SST record from the greater North Atlantic between 1854 and 1912, there are statistically significant negative correlations during the fall months between the oxygen isotope record and SSTs in the western North Atlantic, near the mouth of the Gulf of Maine, as would be expected. There are also statistically significant positive correlations during the fall months between the oxygen isotope record and SSTs in the subpolar gyre region of the North Atlantic. The dipole pattern of correlations between the Gulf of Maine isotope record and SSTs in the greater North Atlantic region very closely resembles that of seawater temperatures resulting from AMOC variability in the North Atlantic, confirming that an oxygen isotope reconstruction in the Gulf of Maine could be a valuable, marine proxy for AMOC variability.

4.3 Future work

The reconstruction of Gulf of Maine seawater temperatures presented in this thesis suggests that oxygen isotopes measured in *A. islandica* shells collected in the Gulf of Maine could be an ideal annually resolved, precisely dated marine proxy for AMOC strength, a proxy that is much needed in order to better understand the North Atlantic and global climate system and predict changes to these systems with increasing greenhouse gases. Having established the viability of this proxy in this thesis, much more work is needed to make the AMOC reconstruction presented here a more robust and useful one.

Most importantly, the record from 1915 to present day needs to be completed so that this reconstruction can be calibrated against long-term, instrumental records to ensure that the oxygen isotope values measured in *A. islandica* shells are a valid proxy for seawater temperatures in the Gulf of Maine and for AMOC variability. Once this calibration is complete, the record can be lengthened to include the last 1000 years. This will provide an unprecedented record of annually resolved AMOC variability. Additionally, water samples from a variety of depths throughout the Gulf of Maine will be collected to create a three-dimensional profile of $\delta^{18}O_w$-salinity relationships in the Gulf of Maine. This will further improve the accuracy with which seawater temperatures can be calculated from oxygen isotope values measured in *A. islandica* shells and consequently the accuracy of the proxy reconstruction of AMOC variability in the North Atlantic.

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